La-Ni-Oxide Films, Fibers and Powders by $La(MOE)_3$–$Ni(acac)_2$ Precursors

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The preparation of $LaNiO_3$, $La_4Ni_3O_{10}$, $La_3Ni_2O_{7-\delta}$ and La_2NiO_4 via La-methoxy-ethanolato–$Ni(acac)_2$ precursor was investigated. From these precursors films, fibers and powders were prepared and heat treated to form $LaNiO_3$ at temperatures as low as 750°C with a heating time of 4 h. The formation of $La_4Ni_3O_{10}$ and La_2NiO_4 was complete at 1,000°C, for 4 h, while monophasic $La_3Ni_2O_7$ required heating to 1,150°C, for 1 h. Pathways yielding various phases were also discussed briefly. The techniques used in this study are TGA, mass-spectroscopy, SEM-EDS, TEM-EDS, powder-XRD, and FT-IR spectroscopy.

Introduction

Lanthanum-nickel-oxides are interesting materials for fuel cells (Matumoto et al., 1975), gas sensors (Obayashi et al., 1976), and for catalytic purposes (Choudhary et al., 1996), as well as for their electrical and magnetic properties (Singh et al., 1994; Sagoi et al., 1993). Their structures are closely related to those of the layered perovskite superconductors. In the La-Ni-O system, $LaNiO_3$ and the homologous series $La_{n+1}Ni_nO_{3n+1}$ have been reported (Mohan Ram et al., 1986). La_2NiO_4 can be prepared in air by repeated grindings and firings of La_2O_3 and NiO at 1,200°C (Odier et al., 1985), while the formation of $LaNiO_3$, which decomposes to NiO and members of the $La_{n+1}Ni_nO_{3n+1}$ series at temperatures above 860°C, needs the addition of a flux (sodium-carbonate) to reduce the reaction temperature (Rakshit and Gopalakrishnan, 1994). To decrease the preparation temperature routes using oxalates (Takahashi et al., 1990), nitrates (Mohan Ram et al., 1986) or inverse microemulsion techniques (Gan et al., 1996) have been used. However, control of the morphology of the final oxide materials, such as formation of films, fibers and high surface area powders, is very limited. In this article, we describe the preparation of La-methoxy-ethanolato–$Ni(acac)_2$ precursor solutions with the La to Ni compositions: 1:1, 4:3, 3:2 and 2:1, and their conversion to gels in the form of films, fibers, and powders. We will also give preparation routes to monophasic materials of the above given compositions, as well as a brief discussion of the pathways yielding the various phases.

Experimental Studies

Equipment used

A Scanning electron microscope equipped with an energy dispersive X-ray spectrometer (SEM-EDS) and a transition electron microscope equipped with an energy dispersive X-ray spectrometer (TEM-EDS) have been used for studying the habitus, metal homogeneity, and crystallinity of the samples. The content of the samples was analyzed with a Fourier transform infrared spectrometer (FT-IR). For studies on the behavior of heating, a thermogravimetric apparatus (TGA) and a mass spectrometer have been used. Identification and determination of the unit cells of crystalline materials was done with Guiner-Hägg focusing powder cameras using Cu $K_{\alpha 1}$ radiation and Si or Al as internal standard (powder-XRD).

Chemicals

The nickel acetylacetonate ($Ni(acac)_2$) was dried at 170°C at 0.1 torr, while the Lantanum metal chips (99.9%) were used as purchased. The methoxy-ethanol (MOEH) was dried with 4 Å molecular sieves, and the toluene was used as purchased. The preparations involving the syntheses of the precursors were made in a glove box with dry, oxygen-free argon.

Preparation of precursors

The lanthanum precursor was prepared by dissolving 10 g of La chips in methoxy-ethanol, with about 1 mg of $HgCl_2$ as catalyst at 100°C during 60 h. The solution formed contained green-black fine particles, which were removed by filtering

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through 0.22 mm filters to yield a clear, pale yellow solution. The concentration was determined gravimetrically on La_2O_3 formed by heat treating known volumes of the solution that had been well hydrolyzed at 1,000°C for 12 h. The procedure was checked out by heat treatments at various temperatures up to 1,150°C and times up to 48 h, in order to ensure that full decomposition into oxide had been achieved. No weight loss in addition to that occurring up to 1,000°C (12 h) was found. The La-methoxy-ethoxide ($La(MOE)_3$) concentration was adjusted to a known concentration of approximately 1.0 M, by the addition of methoxy-ethanol.

Preparation of La-Ni gels

La-Ni gels in the forms of monolithic pieces, fibers, and powders of the La:Ni ratios 1:1, 4:3, 3:2 and 2:1 have been prepared as follows. The 1 M $La(MOE)_3$ solution was added $Ni(acac)_2$ and methoxy-ethanol to yield about 1 M metal (La + Ni) solutions. The solutions were heated at 70°C for 6 h, still in inert atmosphere, which yielded brownish green solutions. Monolithic type green gel pieces were prepared by letting the solutions stand in air and absorb moisture while evaporating. Films were deposited on platinum and quartz substrates by adding the 1-M solution to the spinning (about 5,500 rpm) substrates. Fibers were prepared by dipping a metal tip in a solution, made sticky by evaporation of solvent, and slowly withdrawing it. The gels were studied on their habitus, metal homogeneity and content with FT-IR, TEM-EDS and SEM-EDS.

Heat treatment to form oxides

The heat treatments of the gels to investigate the decomposition and formation of various phases have been performed with a TG apparatus. Samples have been quenched out from different temperatures and been analyzed with powder-XRD and in some cases TEM-EDS. Normally, the heating rate was 5°/min in air. The same heating rate has also been used for the mass spectrometer studies. In the mass spectrometer studies, the atmosphere was 80% helium and 20% oxygen, instead of air. Heating to obtain phase pure La-Ni-O phases has been performed in air at temperatures ranging from 750 to 1,150°C. These materials have been characterized by powder-XRD.

Results and Discussion

Preparation of La-Ni gels

The gels obtained according to the procedure described above were green and consisted of small, dense pieces that could easily be crushed into powders with particles of micrometer sizes. FT-IR spectra of the gels, $Ni(acac)_2$, hydrolyzed $La(MOE)_3$, and MOEH are shown in Figure 1. The gels show spectra with peaks in the same positions, regardless of the composition and the small changes in intensity, are monotonously changing with the composition. Most peaks coincide with those of the pure, dried $Ni(acac)_2$. The main contribution from the La-gel is the broad band ranging from 800 to 450 cm^{-1}, assigned as stemming from La-O stretches and OH modes, and small peaks between 1,150 and 1,050 cm^{-1} and around 850 cm^{-1} that could be attributed to methoxy-ethanolato groups (Figure 1). In addition, absorptions are observed at around 3,400 and 1,600 cm^{-1} assigned as stemming from H_2O and OH groups bonded mainly to La. Thus, it seems as the binary gels are diphasic with one component being $Ni(acac)_2$ and the other one being hydrolyzed $La(MOE)_3$ containing a large amount of hydroxo groups and some methoxy-ethanolato groups.

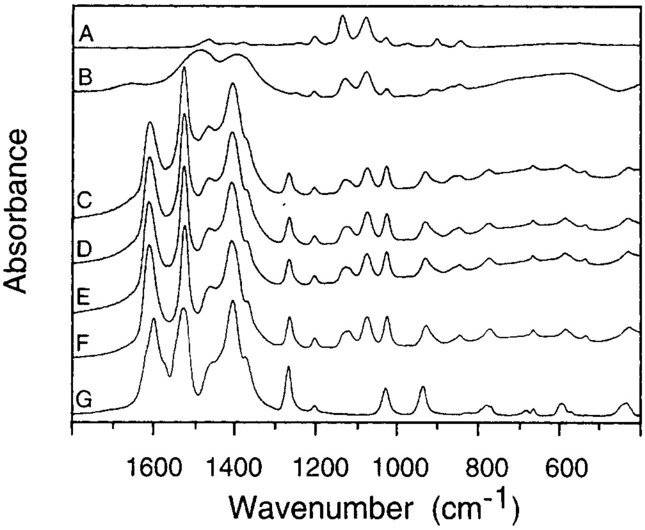

Figure 1. (A) FT-IR spectra of methoxyethanol (MOEH); (B) hydrolyzed $La(MOE)_3$; (C) La-Ni gels with the La:Ni compositions 1:1; (D) 4:3; (E) 3:2; (F) 2:1; and (G) $Ni(acac)_2$.

The TEM-EDS studies showed that the gels were amorphous and homogeneous in their microstructures. They were built up by 20–200-nm strongly agglomerated particles such as those shown in Figure 2. The metal composition varied only with one or two percent over a large number of spot analyses. Thus, if the material consists of two phases, as the FT-IR studies suggest, they must be very intimately mixed, probably on a level less than 4–5 nm, not to be observed with the TEM. A similar gel buildup has been observed for gels

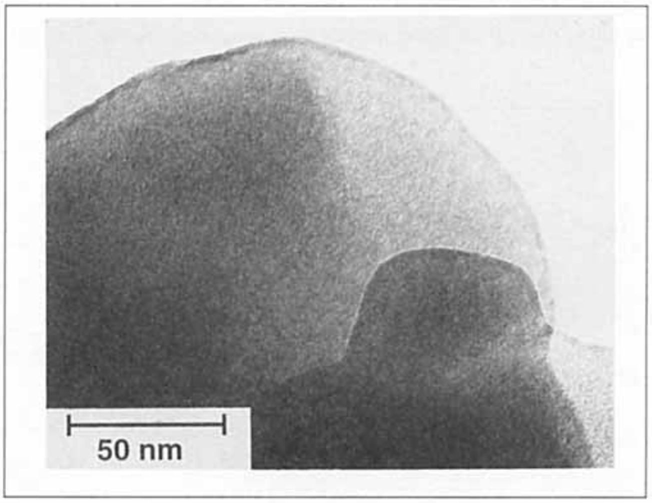

Figure 2. TEM image of La-Ni gel (La:Ni 1:1) showing homogeneous microstructure and strongly agglomerated particles.

prepared from $Ni(OAc)_2$-$Sb(OBu^n)_3$ precursors (Westin, 1994). It is perhaps better to regard these materials as composites rather than gels.

Adding an La-Ni solution to substrates spinning at a rate of about 5,500 rpm yielded green, crack-free thin films. It seems probable that the architecture of these films is similar to that of the monolithic type gels described above. Evaporation of the La-Ni precursor solutions in air yielded just before they got completely dried, sticky solutions. By dipping a metal tip into the solution and slowly pulling it up, it was possible to obtain gel fibers of several centimeters.

Heat treatment to form oxides

Studies of the Conversion of Gel to Oxide. TG curves of the La-Ni gels obtained in air are shown in Figure 3. The decomposition of the organic parts and loss of water and alcohol proceeds up to 800°C for all samples. The decomposition occurs through several small steps which are similar for all compositions. If we are assigning the Ni-component as being $Ni(acac)_2$ (*vide supra*), the La component should correspond to $LaO_{1.5}$ plus a weight of 110–140 mass units, probably in the form of water and methoxy ethanol groups as indicated by the FT-IR studies. The weight loss up to 250°C is probably due to loss of water and alcohol and the mass spectrometer runs showed only a mass corresponding to water in this region. At 250°C, the materials were still X-ray amorphous.

In the region 250–400°C, the weight loss is associated with a decomposition of the acac groups without much combustion and the mass spectrometer runs showed strong peaks typical of decomposed hydrocarbons, while the peaks corresponding to CO_2 were very small. The mass spectrometer runs also showed that some water was evolved, which we believe stem from the La-part of the material.

In the temperature range 450–650°C, the weight loss is ascribed to combustion of the residual organic groups and a strong peak of CO_2 is observed in the mass spectrometer runs. In the two most Ni-rich compositions, we did also observe broad lines matching NiO (Swanson and Tatge, 1953) at 480°C by powder-XRD. At 570 and 680°C, NiO and $La_2O_2CO_3$ (Scharfenberger and Eysel, 1985) were present for all compositions. Thus, it seems that some of the CO_2 evolved in the combustion of the acac groups was absorbed by the La containing phase. The last weight loss occurs in the range 680 to 800°C with evolution of CO_2 according to the mass spectrometer runs and is probably due to thermal decomposition of the $La_2O_2CO_3$ yielding La_2O_3.

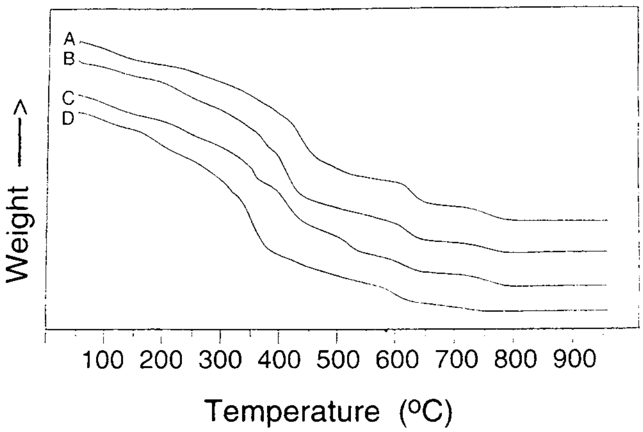

Figure 3. TG-curves of gels with La:Ni compositions: (A) 1:1; (B) 4:3; (C) 3:2; and (D) 2:1.

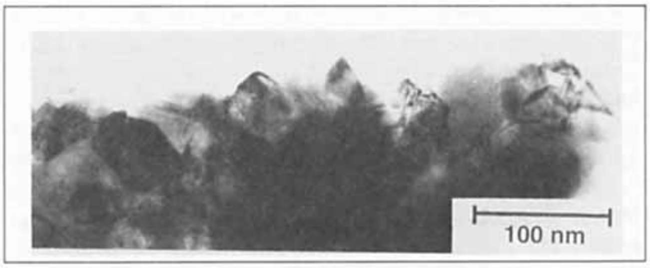

Figure 4. TEM image of the nanocrystalline La_2NiO_4 formed by heat treatment at 5°C/min to 950°C.

At 820°C, the materials consisted, according to the powder XRD studies, of $LaNiO_3$ (Wustenberg and Hahn, 1981) for the two most Ni-rich samples (La:Ni 1:1 and 4:3) and La_2NiO_4 (von Rabenau and Eckerlin, 1958) for the two most La-rich samples (La:Ni 3:2 and 2:1). By TEM studies, we also observed that an amorphous material was present in these materials. Further heating to 950°C did not cause any detectable weight changes and the phases found by powder XRD studies were the same as those found at 820°C, except for the La:Ni (2:1) material, where a small amount of La_2O_3 was found in addition to the La_2NiO_4. The La_2O_3 might stem from a slightly erroneous starting composition. Thus, the first binary oxides to be formed were $LaNiO_3$ and La_2NiO_4. The crystallites were normally of sizes from 10 to 80 nm, as in Figure 4.

Isothermal Heat Treatments. Heating of the samples to 950°C at a rate of 5°C/min, without annealing, yielded materials that contained as crystalline components $LaNiO_3$ or La_2NiO_4, and not the $La_4Ni_3O_{10}$ and $La_3Ni_2O_7$ phases. Therefore, we have annealed the samples at 750, 1,000 and 1,150°C to obtain the pure phases in the same compositions as the starting materials. In Figure 5, the powder X-ray diffractograms are shown for the materials where they first appear as phase pure.

$LaNiO_3$ [$a = 5.451(4)$ Å, $c = 6.57(2)$ Å] was obtained already after annealing at 750°C for 4 h. This phase was decomposed into $La_{n+1}Ni_nO_{3n+1}$ phases with higher La contents and NiO when annealed at 1,000°C. The orthorhombic $La_4Ni_3O_{10}$ (Kitayama, 1990) was first found at 1,000°C, with 4 h annealing. The $La_3Ni_2O_7$ (Kitayama, 1990) was found at 1,000°C, but the material also contained some NiO and La_2NiO_4. Annealing at 1,150°C yielded a phase pure $La_3Ni_2O_{7-\delta}$ with the cell parameters: $a = 5.403(2)$ Å, $b = 5.455(2)$Å; $c = 20.56(1)$ Å). This cell corresponds to a δ of 0.03. The tetragonal La_2NiO_4 [$a = 3.858(1)$ Å; $c = 12.70(1)$ Å] could be obtained already at 750°C, with 4 h annealing, but it was accompanied with a small amount of La_2O_3.

Preparation of Films and Fibers. In practical applications films and fibers are of great interest. We have prepared gel fibers of the La to Ni ratios: 1:1, 4:3, 3:2 and 2:1 and converted them to oxide fibers by heating at a rate of 3°C/min up to 750°C, followed by a 30-min annealing at this temperature. Smooth oxide fibers, as shown in Figure 6, with diameters up to 50 μm and lengths of several millimeters, could be prepared without any special tools. The heat treatment should

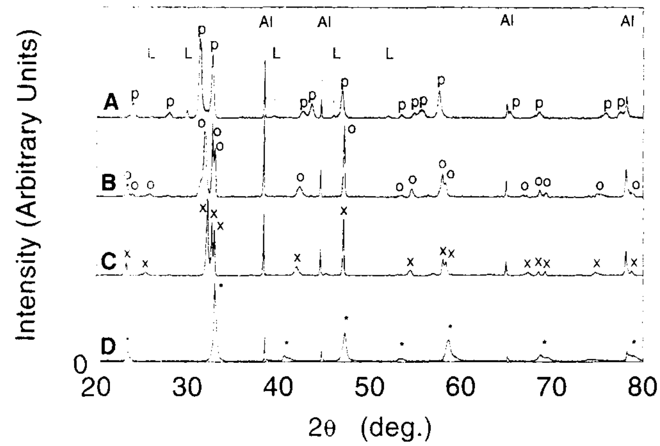

Figure 5. Powder X-ray diffractograms of materials heat-treated at: (A) La:Ni (2:1), 750°C, 4 h; (B) La:Ni (2:3) 1,150°C, 2 h; (C) La:Ni (3:4) 1,000°C, 4 h; and (D) La:Ni (1:1) 750°C, 4 h.

The following phases are marked out: Al (Al standard), *($LaNiO_3$), X ($La_4Ni_3O_{10}$), O ($La_3Ni_2O_7$), p La_2NiO_4 and L (La_2O_3).

be sufficient to yield crystalline $LaNiO_3$ and La_2NiO_4, and the angular protruding parts seen in the oxide fiber are most probably crystallites. These parts are not observed for the gel-fibers or fibers heat treated to lower temperatures.

Gel films that had been prepared by dropping the precursor solution on spinning substrates were transformed to oxide films with the same heat treatment as was used for the fiber preparation. Crack-free films could be prepared with up to 200-nm thickness for each layer. Films with a total thickness of 2 μm were prepared by repeating the deposition and heat treatment several times. When films thicker than 200 nm were deposited, some cracks were formed. These cracks could, however, be filled in to a large extent by adding thinner gel-layers on top of the cracked oxide film, and afterwards annealing them at 800°C.

Conclusions

We have described the preparation of precursor solutions based on $Ni(acac)_2$ and $La(MOE)_3$ with the La to Ni compositions: 1:1, 4:3, 3:2 and 2:1. The precursor solutions have been used to prepare composites of nanometer sized La containing particles and $Ni(acac)_2$ as powders, films, and fibers. The decomposition of these materials to form oxides has been studied and the pure oxides are formed at 820°C, if they are not annealed. Annealings at different temperatures have been made, and the phase pure materials have been obtained at 750°C: 4 h for $LaNiO_3$ and La_2NiO_4 (with a small amount of La_2O_3 present); at 1000°C, 1 h for $La_4Ni_3O_{10}$; at 1,150°C, 1 h for $La_3Ni_2O_7$. These temperatures are quite low compared with the temperatures that are normally used in the synthesis of these compounds, and we have not needed any sintering aids for the densification of the oxide films at 750°C.

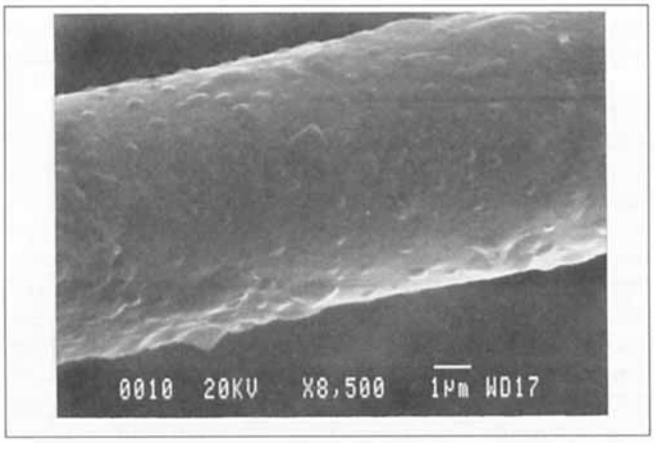

Figure 6. Crystallized oxide fiber of La:Ni (1:1) composition after heat treatment to 750°C.

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