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# Optimization of processing parameters for preparation of $LaNiO_3$ thin films from the citrate precursors

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**Abstract**

Lanthanum nickel oxide ($LaNiO_3$) is an electrically conductive ceramics, which has a potential use as electrode for ferroelectric thin films, multilayer actuators and many other electronic devices. In this work, $LaNiO_3$ thin films were prepared by a modified Pechini process, based on polymeric citrate precursors. DTA analysis of the precursor solution showed that formation and crystallization of $LaNiO_3$ were completed up to 790 °C. Films were deposited using spin-on technique and thermally treated in temperature range 600–800 °C, with heating rate of 1°/min. Processing parameters, such as concentration and annealing temperature, as well as number of deposited layers were optimized to achieve desired film quality. The structure of $LaNiO_3$ was confirmed by X-ray diffraction analysis, whereas microstructural parameters, such as grain size and roughness, were analyzed by AFM.


*Keywords:* Precursors-organic; Films; $LaNiO_3$

## 1. Introduction

Due to its electric,[1,2] magnetic[3] and optical[4] properties lanthanum nickel oxide, $LaNiO_3$, (LNO) has been investigated as material with potentially wide applications. Its low resistivity makes it very promising electrode in ferroelectric devices.[2,5,6] Fatigue problem, which is very common for ceramics films deposited onto platinum electrodes, can be avoided using an oxide electrode like LNO, because it can compensate oxygen vacancies in the ferroelectric films during the fatigue process.[7] This was proved by deposition of many different ferroelectrics, like PZT,[5,7] PLT[5] and PCT[8] prepared on LNO thin films.

LNO thin films can be prepared by various methods. Some physical methods as RF-sputtering,[9] pulsed laser deposition[10] and mist plasma evaporation[11] are good for obtaining epitaxial LNO films on various substrates. Unfortunately, these methods require extreme experimental conditions and complicated techniques, making chemical procedures for preparing thin films with perovskite structure more convenient. Different chemical methods, like sol–gel process,[12] chemical solution deposition[2,5] or metallo-organic decomposition[1] have been reported for obtaining polycrystalline and highly oriented LNO thin films. As a rule, some inorganic and organic salts, like nitrates[2] or acetates[2,5] are previously used as precursors.

The aim of this work was to prepare precursor solution of metal citrates, which will be further used to obtain LNO thin films by spin-on technique. Precursor solution was successfully prepared starting from lanthanum oxide and nickel acetate. The work is focused on determining optimal parameters for obtaining well-crystallized LNO thin films from the citrate precursors.

## 2. Experimental procedure

LNO precursor solution was prepared by modified Pechini method[13] in which separately synthesized lanthanum and nickel citrates were mixed. First, citric acid was added into suspension of lanthanum oxide ($La_2O_3$) in deionized water; the molar ratio of $La^{3+}$ and citric acid was 1:4. After refluxing for 2 h at 120 °C,[14] an amorphous lanthanum citrate was obtained, and then dissolved in aqueous ammonia until pH of the solution was around 7. Nickel citrate was prepared by heating the water solution of nickel acetate [$Ni(CH_3COO)_2{\cdot}4H_2O$] and citric acid (molar ratio of $Ni^{2+}$ and citric acid was 1:4). By mixing two citrate solutions the final precursor solution, with La:Ni molar

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ratio equal to l, was made. To promote the reaction of polyesterification ethylene glycol was added, in a ratio 1:4 with respect to citric acid. The final concentrations of precursor solutions were adjusted to 0.2 and 0.1 M, where latter is prepared by diluting the first solution with ethylene glycol. Viscosity of both solutions was 30 cP.

DTA analysis of precursor solution previously dried at 150 °C, was performed on AMINCO thermal analyzer, with heating rate of 10 °C/min in air atmosphere.

LNO solution was deposited on Pt-substrates using spin-on technique (3000 rpm, 30 s). The substrates were heated with 1 °/min rate and then annealed for 30 min at 600, 700, and 800 °C. For each temperature three samples of different thickness were prepared by depositing from one to four layers of precursor solution.

Microstructure of thin films was analyzed by AFM (Auto-Probe CP Research, TM microscopes) and by scanning electron microscopy (JEOL, model JSM-5300).

X-ray diffraction (XRD) analysis was performed on four layered films using a Siemens D500 instrument, with Ni filtered Cu $K_\alpha$ radiation.

## 3. Results and discussion

Fig. 1 shows DTA curve of dried LNO precursor solution. Two endothermic peaks at 162 and 262 °C are observed. The first peak can be attributed to the evaporation of coordinated water molecules and the second one to the beginning of decomposition of precursor gel and formation of intermediate products like NiO, $La_2O_3$ and $La_2NiO_4$.[15] Exothermic peaks in the region between 300 and 800 °C (centered at 350, 460 and 565 °C) correspond to the complete combustion of organic material and oxidation of intermediate products. In this region the final oxidation of $Ni^{2+}$ into $Ni^{3+}$ takes place. From this analysis it can be concluded that crystallization of $LaNiO_3$ is completed at 790 °C. This is the reason for choosing 800 °C as the first annealing temperature.

The influence of annealing temperature and concentration of precursor solution on the morphology of thin films was studied by AFM. Fig. 2a shows the surface of LNO thin film with

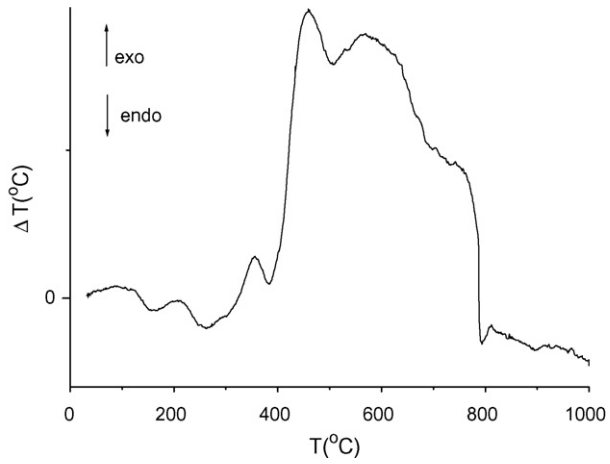


Fig. 1. DTA curve of LNO precursor solution dried at 150 °C.

Table 1
Roughness (nm)/grain size (nm) of the films annealed at 700 and 800 °C

| Annealing temperature (°C) | Number of deposited layers | | |
|---|---|---|---|
| | 1 | 2 | 4 |
| 700 | 5.4/103 | 3.2/71 | 2.9/62 |
| 800 | 5.3/118 | 7.1/118 | 6.4/120 |

two deposited layers prepared from 0.2 M precursor solution and annealed at 800 °C. Thickness of these films was 110 to 310 nm, depending on number of layers. All films prepared from 0.2 M solution, no matter how many layers they have, show well-crystallized grains, but also large cracks.

There are two possible explanations for the existence of the cracks:

- High concentration of precursor solution where metal ions cannot be uniformly arranged within polymeric gel; as a consequence grains do not grow uniformly and cracks appear on the film surface.[16]
- Present amount of ethylene glycol could produce thermal stress in the film.[16]

Decreasing the concentration of precursor solution from 0.2 to 0.1 M by adding ethylene glycol was expected to give better results. In fact, films annealed at 800 °C were dense, crack-free with uniform shape and size of the grains (Fig. 2b). Grain size was about 110 nm (Table 1). SEM micrograph of one-layer LNO film, thermally treated at 800 °C showed the existence of unknown spherical, bright grains on the film surface (Fig. 3). EDS spectra of these grains showed that they are rich in Pt in comparison to the environment. These grains were formed through an interaction between LNO films and Pt layer from the substrate, which is known to occur at higher temperatures.[16,17] Also, EDS spectra of film surface did not show presence of Ni, which can diffuse to the substrate[16] and form intermetallic compound. In order to avoid these undesired processes the annealing temperature was decreased. LNO films prepared from 0.1 M precursor solution and annealed at 700 °C were well crystallized, homogenous and without pores or cracks (Fig. 2c). Film thickness was from 50 to 200 nm depending on number of deposited layers. Grain size of these films was around 70 nm, and films were smooth with Rms roughness of 3 nm (Table 1). On the other hand, films annealed at 600 °C were clearly amorphous showing only beginning of crystallization in some points, but without existence of defined grains (Fig. 2d). This is in accordance with above described DTA results and some previously reported works.[17,18]

XRD analysis also confirmed that films obtained at 600 °C were mainly amorphous (Fig. 4). Only two extremely weak maxima at about 32° and 33° 2$\theta$, indicating the beginning of crystallization, were visible in XRD pattern. Very similar pattern is observed at 800 °C. However, at 700 °C two LNO maxima at 32.12° and 33.12° 2$\theta$ are easily recognized. These results can be explained as follows. The annealing temperature of 600 °C is too low and obtained LNO film is still amorphous. Increas-

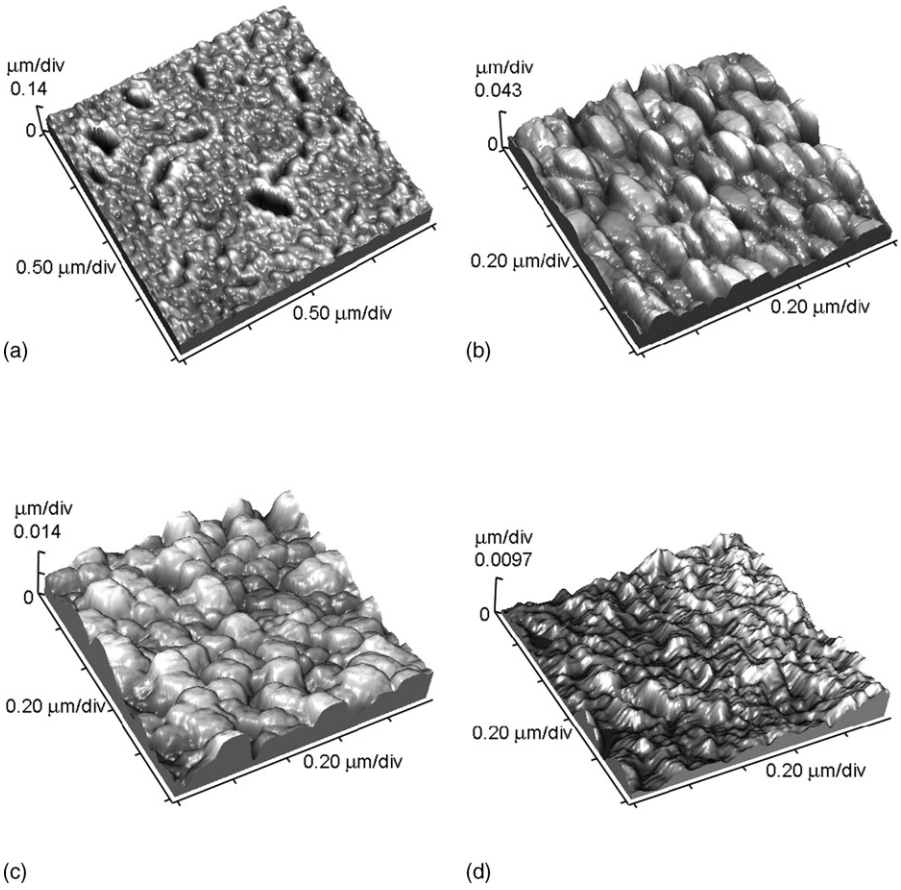


Fig. 2. AFM micrograph of the LNO thin film made from (a) 0.2 M precursor solution and annealed on 800 °C, (b) 0.1 M precursor solution and annealed at 800 °C, (c) 0.1 M precursor solution annealed at 700 °C and (d) 0.1 M precursor solution and annealed at 600 °C.

ing the temperature to 700 °C significantly improves degree of crystallization and results in a high quality LNO film. However, after the further increasing of the temperature to 800 °C the film is again amorphous, because an intensive Pt diffusion toward film surface and Ni diffusion in the opposite direction leads to the degradation of LNO structure.

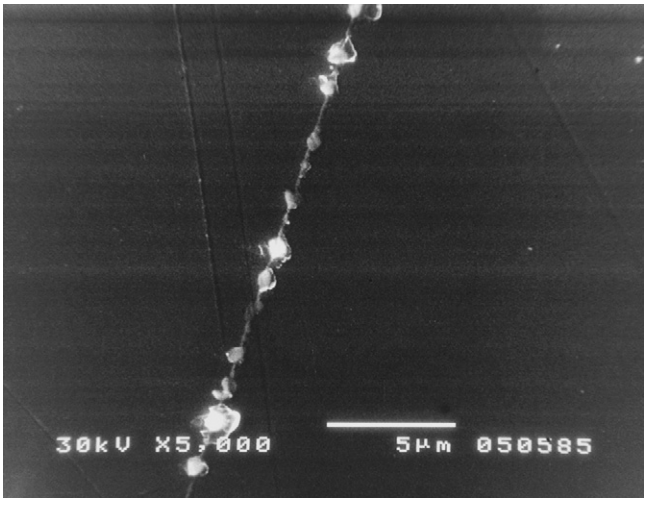


Fig. 3. SEM photograph of platinum grains diffused on the surface of the LNO thin film made from 0.1 M precursor solution and annealed at 800 °C.

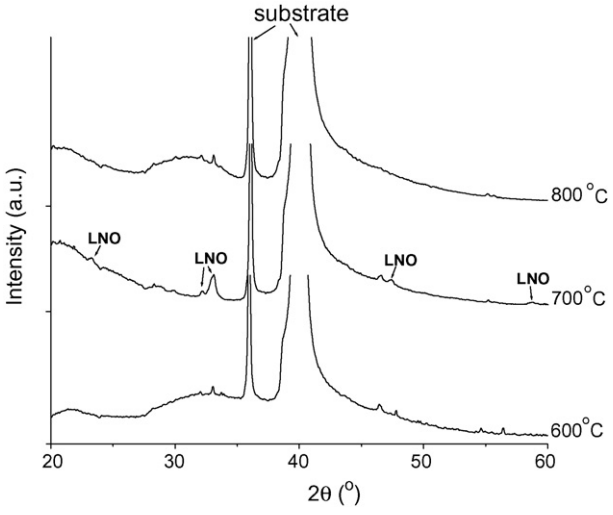


Fig. 4. XRD pattern of the four layered films annealed at different temperatures.

## 4. Conclusions

LNO precursor solution was successfully synthesized starting from citric acid, lanthanum oxide and nickel acetate. This method is very convenient and offers good control of stoichiometry. Higher concentration of precursor solution (0.2 M) yielded thin films with large cracks. Films prepared from 0.1 M

precursor solution and annealed at 600 °C were amorphous. Well-crystallized, dense, crack-free thin films were obtained on platinum substrate from 0.1 M precursor solution with annealing temperature of 700 °C. Films prepared from 0.1 M precursor solution thermally treated at 800 °C were amorphous due to degradation of LNO structure.

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