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Preparation of nanosized perovskite $LaNiO_3$ powder via amorphous heteronuclear complex precursor

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Nanosized lanthanum nickel oxide powder $LaNiO_3$ with perovskite structure was successfully synthesized at a relatively low calcination temperature by using an amorphous heteronuclear complex $LaNi(DTPA) \cdot 6H_2O$ as a precursor. The precursor decomposed completely into nickel oxide above 600°C based on the DTA and TGA results. XRD demonstrated that nanosized $LaNiO_3$ crystalline powder with pure perovskite structure was obtained after the calcination temperature increased to 700°C. The effects of calcination time and temperature were also examined by XRD and TEM. The results indicated the grain size and the crystal size of $LaNiO_3$ increased with the calcination temperature from 600°C to 900°C, and were less influenced by the heat-treatment time. The electrical resistivity of the powder decreased when the calcination temperature increased. It can be concluded that it is a useful way to synthesize nanosized perovskite oxides using an amorphous complex as a precursor, and this method can be easily quantitatively controlled. © *2003 Kluwer Academic Publishers*

1. Introduction

There is growing use of the perovskite type mixed metal oxide materials. The study of preparation routes and properties of them have generated considerable interest in recent years [1–4]. Among these materials, the lanthanum nickel oxide ($LaNiO_3$) class of perovskite is regarded extremely important due to its electronic properties [5, 6]. However, it is one of the materials that have not been studied extensively [7].

$LaNiO_3$ with perovskite structure shows metallic character, which is quite uncommon in oxides. It is well known to be a rhombohedrically distorted perovskite which exhibits a metallic character down to 4.2 K [8]. The electrical and magnetic properties of this oxide are governed by strong electronic correlation effects. Thus it is important to investigate the effect of the preparation route and calcination conditions on the crystalline structure and phase composition of synthesized $LaNiO_3$ materials. These factors are considered important due to their effect on electronic properties, which affect electrical conductivity.

Different preparation methods of the perovskite oxides have been studied in the last decades. The traditional methods included co-melting, freeze-drying, evaporation, Sol-Gel *et al.* The co-melting method by solid state reaction requires a very high temperature [9], and it is difficult to obtain nanosized materials. Literature results have shown the solid-state reaction between the metal oxides of Ni and La only at elevated temperatures of above 1500°C [10]. Sol-Gel and evaporation methods are quite popular to prepare perovskite materials. However, they will result in poor homogeneity and complex multiphase oxide systems [11].

In this work, the nanosized perovskite oxide $LaNiO_3$ was successfully prepared using an amorphous heteronuclear complex as a precursor. The crystalline phase with perovskite structure was obtained after the precursor was calcined at 600°C for 2 hrs. The grain size and crystal size increased with the calcination temperature and time.

2. Experimental section

2.1. Synthesis of $LaNi(DTPA) \cdot 6H_2O$ precursor

Firstly, $La(NO_3)_3 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ powder with a molar ratio of 1:1 were dissolved in distilled water. Then 1.0 mol/l NaOH solution was added in drops into the mixture solution with the desired molar ratio to prepare the fresh $La(OH)_3$, $Ni(OH)_2$ depositions. The depositions were washed by the distilled water by several times to remove the excess OH^-. Then, calculated quantity of H_5DTPA solution, Diethylenetriaminepentaacetic acid, was mixed with these hydroxides for reaction. It was stirred and heated at about 80°C to promote the dissolution and reaction until the mixture became a purple transparent solution mixture.

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After vaporized slowly at room temperature, the solution became a piece of transparent glass-like material. The ICP analysis indicated the molar ratio of La and Ni was 1:1. The possible formula of the precursor was LaNi(DTPA) · $6H_2O$. The XRD pattern demonstrated that the complex precursor was amorphous.

2.2. Preparation of $LaNiO_3$ powder

The $LaNiO_3$ oxide was obtained by decomposing the precursor in air. At first, the temperature was raised to 350°C at a slow heating rate (5–6°C/min). Secondly, keep the sample at this temperature for 90 min to promote the decomposition of organic components. At last, the temperature increased to various pre-set temperatures and maintained for a definite period of time to promote the formation of perovskite-type oxides.

2.3. Analytical techniques

TGA and DTA analyses were performed on Dupond 1090 thermal analyzer. The atmosphere was air and the heating rate was 10°C/min. XRD experiments were carried out in Bruker D8 Advance X-ray Powder Diffractometer with Cu K_α radiation. The surface morphology was measured using Hitachi H-800 Transmission Electron Microscopy (TEM). The accelerating voltage of electron beam was 200 kV. The résistance was measured with a four-probe method in an air flow. The crystalline powder sample was pressed into a slice with a round section of a 15 mm diatmeter and a 2 mm thickness. The measurement experiment was carried in the Potentiostat/Galvanostat electrochemistry analyzer Model 283. The electrical current was 1 mA.

3. Results and discussion

3.1. The thermal decomposition analysis of the precursor

The thermal analysis results of TGA and DTA for LaNi(DTPA) · $6H_2O$ complex are shown in Fig. 1. The TGA curve showed the change of residual weight with temperature, from which four main weight loss regions can be observed. According to the quantitative calculation of the weight loss in each region, the thermal decomposition processes may be distinguished as followings. The weight loss region from 40 to 150°C was caused by the loss of coordinated water. The region from 208 to 300°C mainly resulted from the decomposition of some organic groups, including the decomposition of hydrocarbon, amino-group organic compounds. The 300 to 350°C one was attributed to the disconnection of the bond between metal and carboxyl of the precursor. And the last one from 350 to 450°C was caused by the formation of the oxides. All organic components could been eliminated at 550°C because there was no future weight loss region. On the DTA curve two exothermic peaks were observed. The little endothermic peak at 355°C was attributed to the loss of some organic groups such as amino-group and hydrocarbon group. The other exothermic peak at 478°C was strong and very sharp. This peak was considered as the decomposition of the precursor and the formation of the crystal structure of $LaNiO_3$, which was related with the fourth weight loss region. The results above suggested that $LaNiO_3$ oxide can be formed above 550°C by decomposing an amorphous complex of LaNi(DTPA) · $6H_2O$.

3.2. The formation of $LaNiO_3$ crystal structure

3.2.1. Influence of calcination temperature on sample crystallization and electrical resistivity

The effect of the calcination temperature on the formation of $LaNiO_3$ crystalline phase has been investigated by XRD. The XRD patterns of $LaNiO_3$ sample calcined at different temperature are shown in Fig. 2. After the amorphous precursor was calcined at 500°C for 2 hrs, the production of some $La_2O_2CO_3$ [12] species with little $LaNiO_3$ was obtained, indicating the decomposition of the precursor was incomplete at that temperature. When the temperature raised to 600°C, the peaks of $La_2O_2CO_3$ disappeared and a perfect perovskite crystalline phase of $LaNiO_3$ [13] formed. Another phase of $La_8Ni_4O_{17}$ [14] was also obtained. But they were minor. Since a Ni deficient phase was observed, some

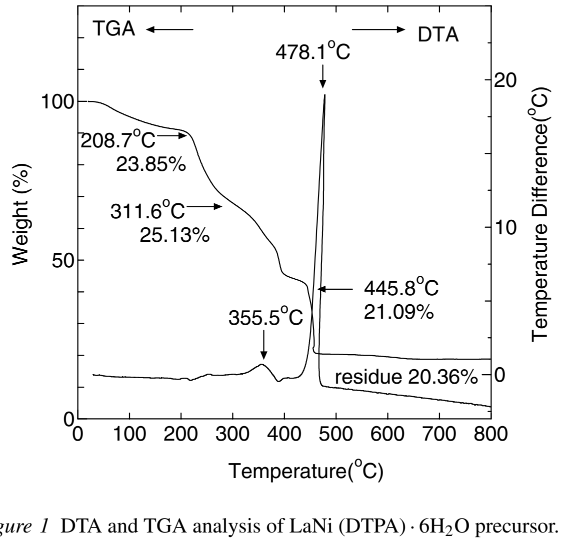

Figure 1 DTA and TGA analysis of LaNi (DTPA) · $6H_2O$ precursor.

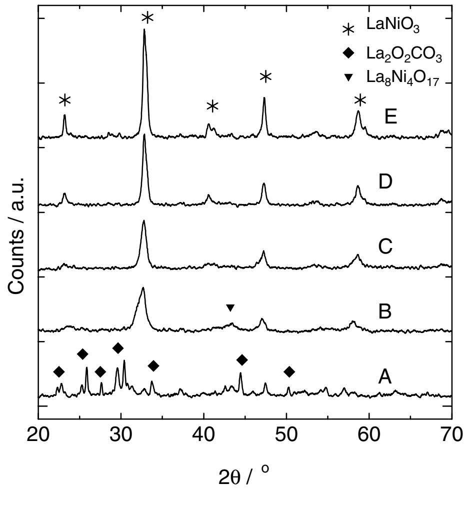

Figure 2 XRD pattern of $LaNiO_3$ powder calcined for 2 hrs at different temperature: (a) 500°C, (b) 600°C, (c) 700°C, (d) 800°C, and (e) 900°C.

other phase of Ni oxide must exist. They were not observed by the XRD because they were amorphous or were present in crystalline form but in insufficient quantity of be detected. As to 700°C, no other peaks were observed except the perovskite structure peaks of $LaNiO_3$. With the calcination temperature rising, the peaks of the perovskite structure intensified significantly and became sharper, suggesting that the crystalline phase of $LaNiO_3$ became more perfect. The temperature of complete decomposition was higher than that of TGA-DTA results because the quantity of TGA-DTA was much less. The precursor of large amount couldn't decompose in just 2 hrs. It was believed that it would decompose completely if the calcination time was prolonged enough long. The above results showed that the rising calcination temperature can promote the crystallization process.

The crystal sizes of the $LaNiO_3$ powder can be measured from the XRD patterns based on the Scherrer equation $D = k\lambda/\beta\cos\theta$. D was the crystal size, θ was the diffraction angel, β was the width of the peak and the value of k was 0.89. The results were shown in Fig. 3. It showed the crystal size of the powder increased from 12.0 to 29.8 nm with the calcination temperature. The activation energies of crystal size growth can be calculated according to the Burke equation: $D^2 - D_0^2 = K_0 t^n \exp(-Q/RT)$. It was obtained that the activation energies of the crystal size growth were 50.7 kJ $\cdot$ mol^{-1} for the sample.

Fig. 4 showed the influence of the calcination temperature on the resistivity of $LaNiO_3$ powder. The electrical resistivity decreased with the increase of calcination temperature from 550 to 800°C, indicating the resistivity dropped rapidly with the formation of the perovskite structure. The electrical resistivity of the sample calcined at 550°C was much larger than the others. The reasons can be seen from the XRD results (shown in Fig. 5): some other phase (such as $La_8Ni_4O_{17}$) existed and the $LaNiO_3$ perovskite phase was not perfect. There is some decrease of the electrical resistivity of 600°C sample because the crystal structure of $LaNiO_3$ became more perfect. The resistivity of pure-phased 700°C sample dropped dramatically, suggesting the perovskite structure of $LaNiO_3$ had a good electrical conducting performance. Once the perfect perovskite structure was obtained, the electrical resistivity didn't change much. The minimum electrical resistivity was $0.071\,\Omega\cdot\text{cm}$. The fact that the electrical resistivity of the samples decrease with the increase of the calcination temperature mainly resulted from the more perfect crystalline structure. The above results showed that the formation of perovskite structure had an important effect on the electrical resistivity of the powder $LaNiO_3$ sample.

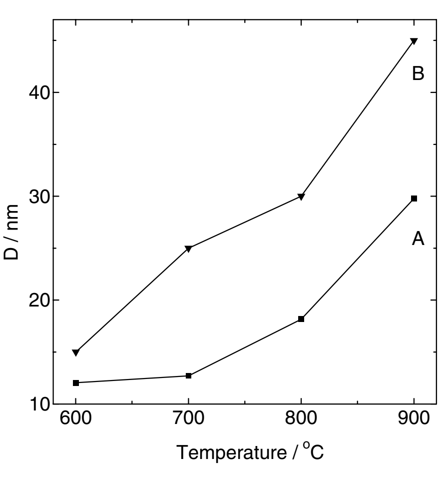

Figure 3 The dependence of the crystal size and grain size of the powder sample on the calcination temperature: (a) crystal size and (b) grain size.

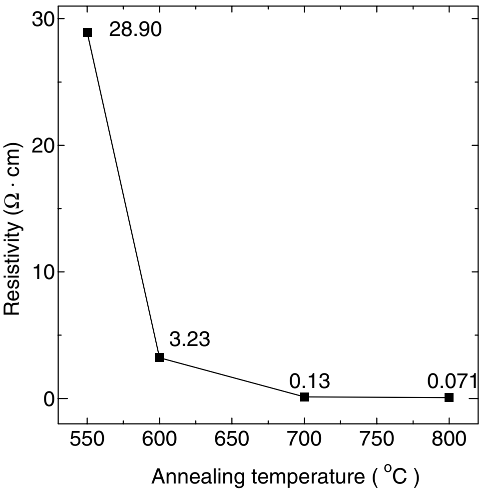

Figure 4 The electrical resistivity of $LaNiO_3$ powder calcined at different temperatures.

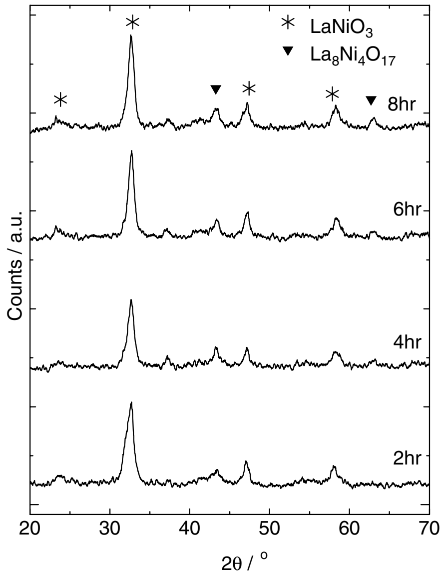

Figure 5 XRD pattern of $LaNiO_3$ powder calcined at 550°C for different time.

3.2.2. Influence of calcination time on crystallization

Fig. 5 shows the influence of the calcination time on the formation of $LaNiO_3$ crystal phase. The calcination temperature was defined 550°C because the perovskite structure of the sample formed between 500 and 600°C. After the sample calcined at 550°C for 2 hrs, a perovskite crystalline phase was formed. Some peaks of $La_8Ni_{14}O_{17}$ were also observed, but the peak was minor. It showed the existence of some other species when the calcinations temperature was low. The crystal structure of $LaNiO_3$ became more perfect when the calcination time was prolonged, although the peaks didn't change significantly. This result indicated the calcination time had a less important effect on the crystallization process.

The above results illustrated that $LaNiO_3$ crystalline phase can be formed at a relatively low temperature (600°C) and for a short time (2 hrs) by using an amorphous complex as a precursor. The influence of the calcination temperature was more significant than that of the calcination time on the formation of the crystalline phase.

3.2.3. The morphology of $LaNiO_3$ powder

The influence of the calcination temperature and time on the grain size of $LaNiO_3$ compound has been investigated by TEM, as shown in Figs 6 and 7. In Fig. 6, it can be seen that some particles of about 10 nm was obtained and some other phases are present. It was consistent with the XRD results and thus the particle was mainly $La_2O_2CO_3$. The other phases are resulted from the incomplete decomposition of the precursor sample. When the calcinations temperature increased to 550°C, the grain size grew larger (about 15 nm). Some particles of $LaNiO_3$ were obtained. When the sample was obtained at a higher calcination temperature such as 600°C, the grain size became homogenous but still fairly small (about 15 nm). The grain size grew quickly from 25–45 nm when the temperature raised from 700 to 900°C. The grain sizes measured from TEM photos are compared with the crystal sizes calculated from XRD patterns, as shown in Fig. 3. Both of them increased with the calcination temperature. The grain sizes were larger than the crystal sizes because the particles were made of several crystallites.

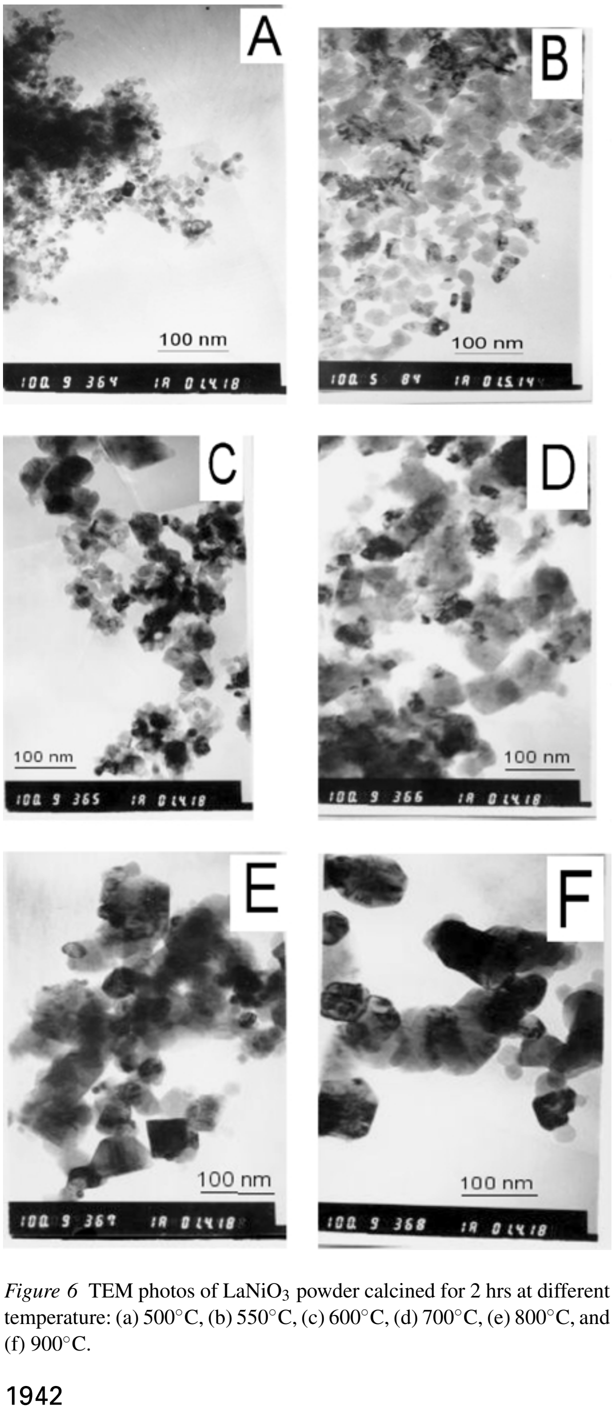

Figure 6 TEM photos of $LaNiO_3$ powder calcined for 2 hrs at different temperature: (a) 500°C, (b) 550°C, (c) 600°C, (d) 700°C, (e) 800°C, and (f) 900°C.

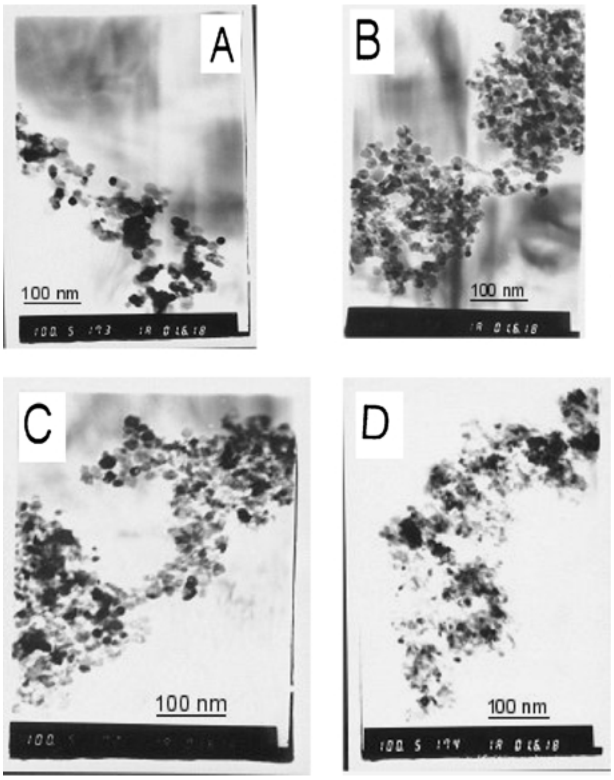

Figure 7 TEM photos of $LaNiO_3$ powder calcined at 550°C for different time: (a) 2 hrs, (b) 4 hrs, (c) 6 hrs, and (d) 8 hrs.

The influence of the heat-treatment time on the average grain size was studied at 550°C for 2, 4, 6, 8 hrs respectively. Fig. 7 showed that the grain sizes were around 15 nm. When the heat-treatment time increased, the grain size changed little. The above results indicated that the effect of calcination temperature on the grain size of $LaNiO_3$ was more serious than that of time.

4. Conclusions

(1) Nanosized $LaNiO_3$ powder with perovskite structure was synthesized using amorphous heteronuclear complex $LaNi(DTPA) \cdot 6H_2O$ as a precursor at a relative low calcination temperature of 600°C. It was an effective method to synthesize nanosized $LaNiO_3$ oxide using amorphous heteronuclear complex as a precursor.

(2) The crystal and grain size grew dramatically with the calcination temperature while the calcination time had little influence.

(3) The electrical resistivity of the powder decreased when the calcination temperature increased. The formation of perovskite structure had an important effect on the electrical resistivity of the powder $LaNiO_3$ sample.

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