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Preparation of $LaNiO_3$ powder from coprecipitated lanthanum–nickel oxalates

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Coprecipitation of lanthanum and nickel oxalates in a water–alcohol mixed solution of an oxalic acid resulted in a simultaneous and homogeneous deposition of the respective oxalate particles with a desired cation ratio. The coprecipitated oxalate could be readily converted to a fine powder (5 to 6 $m^2 g^{-1}$) of the desired $LaNiO_3$ by heating at 800 to 850° C. Detailed examination of some precipitation conditions established an optimum procedure needed for the powder synthesis of $LaNiO_3$. Thermal analysis showed that La_2NiO_4 (high temperature form) is transiently produced prior to the formation of $LaNiO_3$. Mixed valency of the nickel ion in the synthesized powders was quantitatively determined by means of the oxidation–reduction titration, suggesting that the chemical formula of the powders might be $LaNiO_{2.85\,\mathrm{to}\,2.90}$.

1. Introduction

There has been considerable interest in the highly conducting perovskite-type oxides of $LaBO_3$ containing a transition-metal ion as B-site cation [1]. Characteristic aspects of the perovskite structure lie in the flexibility of the crystal structure itself: i.e. partial substitution of each cation site by some foreign cations with different valencies produces an abnormal or mixed valency state and alternatively a lot of oxygen vacancies in the structure. The creation of the abnormal valency state, for instance unstable Co^{4+} in $La_{0.5}Sr_{0.5}CoO_3$ [2], could be due to the compensation of deviated electrical charge arising from cation substitution. Similarly, the mixed valency of B-site cation (Fe^{3+} and Fe^{4+}, for example) could be observed in the cation-substituted solid solution of $La_{1-x}Sr_xFeO_3$ [3].

Among the $LaBO_3$ type compounds, $LaNiO_3$ showing Pauli paramagnetic and metallic properties [4–6] is the most sensitive to oxygen partial pressure in the surrounding atmosphere at elevated temperatures [7]. Since Ni^{3+} in $LaNiO_3$ can be partially reduced to Ni^{2+} in air to produce oxygen vacancies, the composition of the double oxide might be represented as $LaNiO_{3-\delta}$. Oxygen ions in such a perovskite-type oxide are generally very mobile [8, 9]. Therefore, this offers to $LaNiO_3$ a mixed ionic–electronic conducting property, leading to extended applications as an oxygen ion conductor in addition to a metallic one. In fact, promising applications such as electrodes for batteries and fuel cells at high temperatures [10], catalyst [11, 12], or alcohol sensors [13] have been examined. The pure $LaNiO_3$ phase, however, cannot be stable in air above 860° C [1]. It gradually decomposes to the lower oxide $La_{n+1}Ni_nO_{3n+1}$ at higher temperatures [14–16], and finally into the two-dimensional La_2NiO_4 above 1200° C. Thus the very limited region of thermal stability for $LaNiO_3$ provides severe restriction for the synthetic conditions of pure $LaNiO_3$ powder.

Vidyasagar *et al.* [17] have reported the preparation of $LaNiO_3$ powder by starting with hydroxide solid solution precursor and heating the precursor at very low temperature (350° C). However, powder properties of the synthesized materials such as degree of crystallization, specific surface area, etc., have not been found in the literature. The $LaNiO_3$ powders prepared by flux method have only a low value of specific surface area [12]. In the present study, an attempt to prepare a fine, single-phase powder of $LaNiO_3$ was made by using coprecipitated precursors of metal oxalates. No fine powder of the pure material has been successfully synthesized from coprecipitated metal oxalates, mostly due to segregated precipitation of different solid particles. We next developed the coprecipitation process needed for a simultaneous precipitation of both metal cations included in an original solution with a theoretical cation ratio. After detailed examination of the precipitation conditions, we established the appropriate preparation technique for controlling the chemical composition and homogeneity in the coprecipitated oxalates. Finally, some powder properties of the synthesized powders were also investigated.

2. Experimental procedures

2.1. Preparation of mixed oxalates

Coprecipitation of both La and Ni oxalates was performed in the following manner. The required amounts of the hydrous chlorides of the corresponding metals were dissolved in distilled water. The total concentration of a mixed chloride solution,

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$[M]_{total} = [LaCl_3] + [NiCl_2]$, ranged from 0.1 to 0.9 M. Various oxalic acid solutions (0.2 to 1.2 M) used for a precipitating agent were prepared by dissolving oxalic acid (reagent grade) into mixed solvents consisting of distilled water (DW) and some kinds of alcohol (AL) with mixing volume ratios, [AL]/([DW] + [AL]), ranging from 0 to 1.0. Hereafter, oxalic acid solutions used can be distinguished by a shortened letter, for example, MA0.5-solution denoting an oxalic acid solution prepared using a mixed solvent of distilled water and methylalcohol with a volume ratio of 1 : 1. Thus EA, PA, and BA correspond to ethyl, *n*-propyl, and *n*-butyl alcohol, respectively.

Mixing to both starting solutions in an optimum procedure, specified in the next section, resulted in the instantaneous precipitation of metal oxalates. The coprecipitated oxalates were filtered, washed with distilled water, and then oven-dried. The oven-drying was succeeded by heat treatment in the range 200 to 900° C for different periods. Solid phases of oven-dried and thermally treated samples were identified using conventional X-ray diffractometry (XRD). The particle size and shape of the powdered samples were observed by scanning electron microscopy (SEM). Specific surface areas of some selected samples were determined using BET method from N_2 gas adsorption at liquid nitrogen temperature.

2.2. Quantitative analysis of trivalent nickel cation by oxidation-reduction titration

Because the nickel ion in the $LaNiO_3$ structure might exist in more than one oxidation state, a procedure based on an oxidation–reduction reaction can be used to determine the amount of Ni^{3+} cation in $LaNiO_3$ powders synthesized in the present study. The required amount of KI (~ 0.2 g) was dissolved in 25 cm^3 of HCl solution (12N) and 0.250 g of $LaNiO_3$ powder was added to the solution and completely dissolved. This was followed by the addition of distilled water to give a total volume of 150 cm^3. During this process, the Ni^{3+} cation which is a strong oxidizing agent in a solution, is immediately reduced to the Ni^{2+} cation by gaining electrons, whereas the I^- anion in the solution loses electrons to become I_2 which is liberated. Subsequently the amount of liberated I_2, which directly corresponds to that of the Ni^{3+} cation, was quantitatively determined by oxidation–reduction titration using standardized sodium thiosulphate as a titrant.

To avoid atmospheric oxidation of the I^- anion in a starting solution, the analytical operations described above were performed in a flowing atmosphere of dry nitrogen throughout the experiment. The equivalence point in the titration was detected by a change in the colour of oxidation product, the liberated I_2. When the equivalence point was reached, a dark purple solution into which 2 cm^3 of starch solution had been added prior to reaching the final point was decolourized. The fractional content of the Ni^{3+} cation in a sample powder was calculated from an equation, $[Ni^{3+}]/([Ni^{3+}] + [Ni^{2+}]) = (M/W) \times fV$, where M is the molecular weight of $LaNiO_{3-\delta}$, W the sample weight of the powder, f a factor associated with a standard solution of sodium thiosulphate, and V the volume of the standard solution needed to reach the equivalence point.

3. Results and discussion

3.1. Coprecipitation of mixed oxalates in water–alcohol mixed solvents

An instantaneous precipitation of the hydrous lanthanum oxalate, $La_2(C_2O_4)_3 \cdot 10H_2O$, occurs when a 0.4 M aqueous solution of lanthanum chloride (100 cm^3) is added to 200 cm^3 of a vigorously stirred solution of 0.35 M oxalic acid. The crystallinity of the precipitate is lowered with an increasing pH in an oxalic acid solution. A lanthanum oxalate precipitated at pH = 10 shows gel features in its XRD pattern. The precipitation of $NiC_2O_4 \cdot 2H_2O$, on the other hand, is different in nature; it has an induction period with a slower rate of deposition. The delayed rate of substitution with oxalic radicals is mostly due to the formation of a soluble complex species of $Ni(H_2O)_6^{2+}$ in an aqueous solution. In the present coprecipitation system, therefore, a heterogeneous deposition with extended segregation of different kinds of oxalate particles, which could be attributable to occurrence of the delayed precipitation of the nickel oxalate, might be predicted. Generally, stoichiometric deposition of different chemical species with a homogeneous dispersion in a solution system is essential for a coprecipitated precursor leading to the formation of a required, single-phase compound. The difficulty for yielding homogeneous and stoichiometric coprecipitation of unlike oxalates was similarly found in the powder preparation of $LaCoO_3$ [18]. Some portion of a chemical species containing the cobalt cations still remained in a supernatant liquid, in spite of an excess of oxalic acid added to complete the deposition of the cobalt oxalate.

The fractional content of different cations in a coprecipitated oxalate could first be adjusted in the same way as that employed in the preparation of Mg–Mn–Fe ferrite from the corresponding mixed oxalate [19]. That is, the pH control during successive coprecipitation which was combined with a varied concentration of the respective cations in a starting solution, produced a coprecipitated oxalate having a desired composition. This result, however, could not be satisfactorily reproduced in the present study. Next, a reduction or, if possible, a disappearance of an induction period associated with the formation of the nickel oxalate was examined in order that the cation fraction present in a starting solution could be stoichiometrically maintained in a coprecipitated oxalate. An increase in both pH and temperature of oxalic acid solutions remarkably reduced the induction period, but this was insufficient for an instantaneous and complete deposition of the nickel oxalate. For further improvement of the precipitation of the nickel oxalate, the ionic strength of the soluble complex in a starting solution of the mixed metal chlorides was varied by the employment of mixed solvents consisting of distilled water and different kinds of alcohol for oxalic acid solution. In MA-solution, the induction period was found to be of the same duration as that observed in the original solution (≈ 20 min). A very marked reduction effect on the induction period appeared in

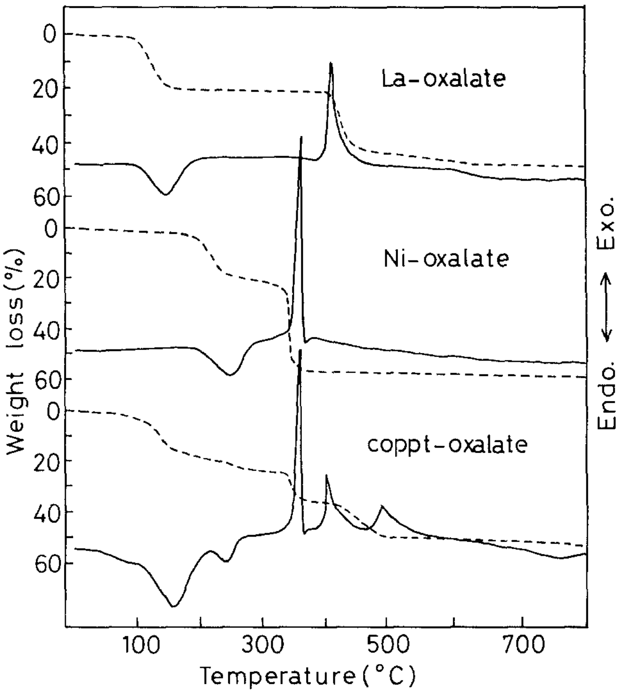

Figure 1 DTA–TG curves of precipitated oxalates.

the case of the other mixed solvents with mixing ratios [AL]/([DW] + [AL]) higher than 0.5. Deposition of the nickel oxalate in a mixed solvent having the ratio of 1.0 yielded an extremely viscous dispersion, resulting in poor deflocculation of the precipitate during successive stirring.

The unlike metal oxalates were coprecipitated in the same oxalic acid solutions as those used in a preliminary examination of the precipitation of nickel oxalate. Fig. 1 shows the results of the thermal analysis for a coprecipitated oxalate and each of the individual precipitates which were formed in an EA0.5-solution. Exothermic peaks at ≈400 and ≈360° C for lanthanum oxalate and nickel oxalate, respectively, correspond to the oxalate decomposition followed by the atmospheric oxidation of carbon monoxide. Similarity of the DTA curves among those samples in Fig. 1 indicates that the coprecipitated oxalate is a mixture of the corresponding metal oxalates. The morphologies of those oxalate powders are presented in Fig. 2. The scanning electron microphotographs reveal different characteristic features for each sample: rod-like particles for the lanthanum oxalate, very fine powder for the nickel oxalate, and aggregated powder consisting of primary particles less than 1 μm for the mixed one.

Table I shows the crystalline phases produced by heating the mixed oxalates, which were coprecipitated in various oxalic acid solutions, at 800° C for 24 h. As has been expected, the formation of the single-phase $LaNiO_3$ powder seems to be closely correlated with the induction period present in the precipitation of nickel oxalate. That is, the undesirable La_2NiO_4 phase appears for the heated samples of the mixed oxalates obtained in mixed MA-solution (all concentrations), and EA- and PA-solutions ([AL]/([DW] + [AL]) < 0.3) of the oxalic acid. The presence of the induction period obviously causes the nonstoichiometric deposition of the unlike metal oxalates. Thus the precipitation rate of the oxalate of the transition metals such as nickel, cobalt and so forth could be extremely accelerated by proper selection of the solvent for a precipitating agent. In the present coprecipitation system, an instantaneous and concurrent precipitation of the lanthanum and nickel oxalates substantially

TABLE I Solid phases produced after heating at 800° C for 24 h for coprecipitated oxalates obtained in different oxalic acid solutions

Mixed solvent	Volume ratio of each alcohol (%)			
	30	50	70	100
MA	L_2N	L_2N	L_2N	–
EA	L_2N, LN	LN	LN	LN, (N)
PA	L_2N, LN	LN	LN	LN, (N)

Solid phases; L_2N = La_2NiO_4, LN = $LaNiO_3$, (N) = NiO_{tr}.

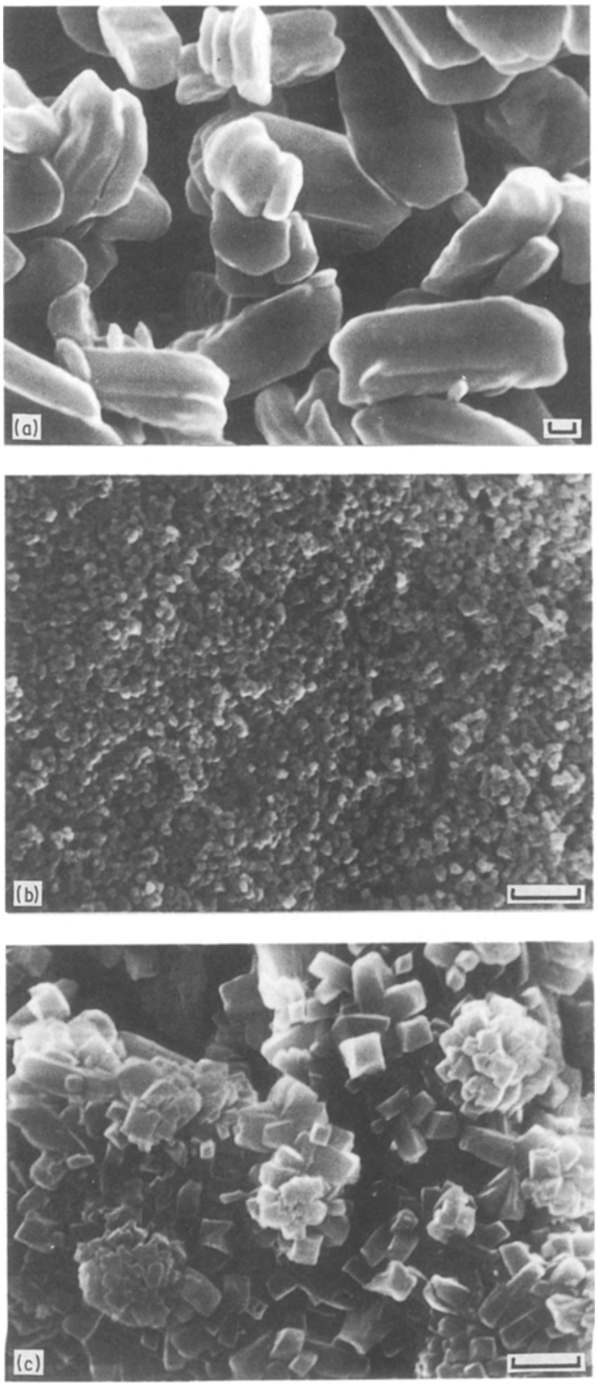

Figure 2 Scanning electron microphotographs of (a) La-oxalate, (b) Ni-oxalate and (c) coprecipitated oxalate. (bar = 1 μm).

improves the stoichiometry in the coprecipitated oxalate, which results in the formation of the required single-phase powder of $LaNiO_3$.

3.2. Coprecipitation behaviours of mixed oxalates under various precipitation conditions

Very rapid coprecipitation technique used in the present study, however, accompanies another problem concerning the segregation of the precipitated constituents. Although the segregated precipitation is more or less inevitable for the coprecipitation of such a mixed oxalate, it can be minimized by employing an optimum precipitation procedure. Several mixing methods of each starting solution combined with a variation in the concentration of different chemical species in the solutions were therefore examined. They were as follows: a voluminous solution of mixed metal chlorides was added as rapidly as possible in oxalic acid solution (method A); a droplet of the mixed chloride solution was constantly added or sprayed into a vigorously stirred solution of the oxalic acid (methods B and C, respectively); and constant streaming fluxes of individual starting solutions were directly contacted near the outlet of a cylindrical separatory funnel (method D).

The coprecipitation experiments described above were conducted in a EA0.5-solution. For the coprecipitated oxalates obtained by methods B and C, XRD analysis of samples heated at 800° C for 24 h in air indicates the appearance of appreciable amounts of the unreacted La_2O_3 and NiO. The single-phase powder of the $LaNiO_3$, on the contrary, is found to be produced in the case of methods A and D. Method D is a superior technique for obtaining reproducibly the homogeneous coprecipitation of unlike metal oxalates, if a constant flux of each solution to be reacted can be steadily supplied. In general, the alternative method, method A, is recommended for the coprecipitation of the mixed oxalate on a laboratory scale. It is concluded that the conventional rapid mixing might maintain a chemical homogeneity existing in a starting solution in the coprecipitated oxalate with minor segregation.

A highly concentrated starting solution is occasionally used to obtain a very fine and highly reactive powder by coprecipitation technique. Since the precipitation characteristics of the lanthanum and nickel oxalates are essentially different, there must be an optimum concentration range for the present starting solutions. In a serial examination of the coprecipitation of the mixed oxalate with varying concentrations of each starting solution, an EA0.5-solution is also used as a mixed solvent for an oxalic acid solution. The results obtained are shown in Fig. 3 where solid phases formed during heat treatment at 800° C for 24 h, i.e. the $LaNiO_3$ without any other phase (○), with small amount (◑), and a large amount (△) of the unreacted La_2O_3 and NiO, are presented with changes in the concentration of each starting solution. In the region surrounded by a solid line, the coprecipitated metal oxalates can be converted to $LaNiO_3$ powder with high reproducibility. (The broken and dotted lines, respectively, denote the La_2O_3-rich and the NiO-rich regions, indicative of the compositional deviation from the stoichiometry in the coprecipitates.) As clearly seen from this figure, the simultaneous deposition of the unlike metal oxalates with minor segregation is difficult to achieve when condensed oxalic acid solutions higher than ≈ 1.1 M or mixed chloride solutions having a concentration higher than ≈ 0.6 M are used for the coprecipitation. Hence the recommended procedure is to prepare an aqueous solution of the mixed chlorides having a total concentration of 0.2 to 0.6 M and an oxalic acid solution in a concentration range 0.4 to 1.0 M for which a mixed solution of distilled water and ethyl alcohol with a volume ratio of 1 : 1 is used as a solvent, and then to contact voluminously both starting solutions while stirring vigorously.

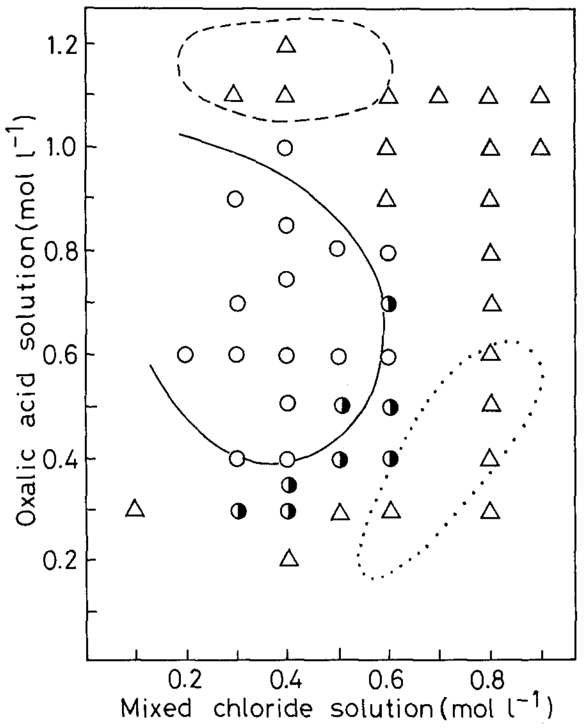

Figure 3 Concentration effect of each starting solution on the formation of $LaNiO_3$ powder.

3.3. Thermal decomposition of coprecipitated oxalate

As shown in Fig. 1, the thermal decomposition behaviour of the mixed oxalate which was coprecipitated under the optimum conditions established in the previous section agrees well with the combined decomposition behaviour of the individual metal oxalates. The dehydrated lanthanum oxalate can be converted to the corresponding oxide in the temperature range 400 to 500° C, according to the following general decomposition scheme; $La_2(C_2O_4)_3 \rightarrow La_2O_3 + 3CO + 3CO_2$. The oxide formed is very unstable and readily adsorbs the carbon dioxide in the atmosphere to produce the carbonate oxide [20] ($La_2O_3 + CO_2 \rightarrow La_2O_2CO_3$). This is confirmed by XRD analysis in the present study. A strong exothermic peak at ≈ 350° C of the coprecipitated oxalate corresponds to the decomposition of the anhydrous nickel oxalate to the oxide in air. The exothermic character arises from the oxidation of the nickel metal which is the primary product of decomposition [21].

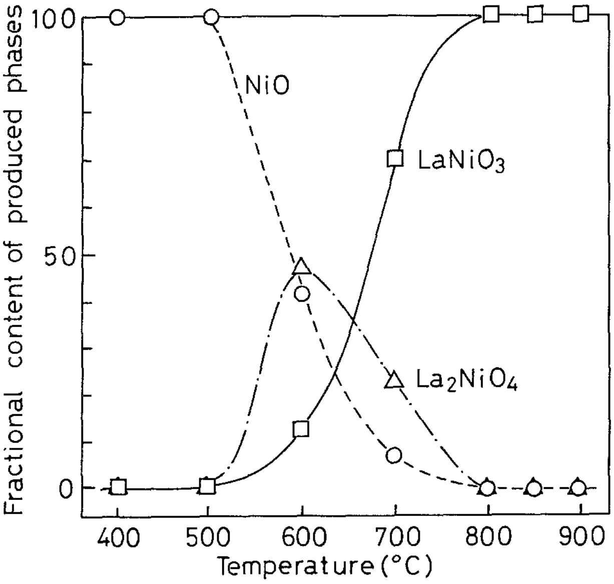

Figure 4 Phase change during heat treatment of coprecipitated oxalate.

Phase changes of the coprecipitated oxalate with thermal treatment in the range from 400 to 900° C are shown in Fig. 4. The fractional content of each produced phase (ordinate) is calculated from the relative intensity change of phases present in XRD patterns of different samples heated at each temperature for 24 h. The formation of the $LaNiO_3$ initiates at around 600° C and is completely accomplished by heating at 800° C for 24 h. It is of great interest to note that before the completion of the formation, La_2NiO_4 transiently appears in the temperature range 600 to 700° C. This compound belongs to the K_2NiF_4 family [22] in which layers of perovskite-type $LaNiO_3$ are present between rock salt-type LaO layers, and are in stable phase above 1200° C in an equilibrium state of the La–Ni–O system [1]. A DTA curve of the coprecipitated oxalate reveals an exothermic peak at $\approx 500°$ C (Fig. 1), which is absent for the individual oxalates precipitated separately. A very broad peak identifiable with the La_2NiO_4 phase appeared in a XRD profile of the heated sample (600° C) of a mechanical mixture of each oxalate, although no such exothermic peak was shown in a DTA analysis of the physical mixture. Therefore, the exothermic peak at $\approx 500°$ C seems to be associated not with the direct formation of the $LaNiO_3$ but with the production of an intermediate oxide phase, La_2NiO_4. The appearance of the exothermic peak in the coprecipitated oxalate is clearly explained by the intimate mixing of very fine particles of each precipitated oxalate. The results obtained suggest that the La_2NiO_4 phase is metastably formed prior to the synthesis of the required $LaNiO_3$ during thermal decomposition of the coprecipitated oxalate.

Fig. 5 shows an isothermal formation behaviour of $LaNiO_3$ after heating up to 800° C with a heating rate of 100° C h^{-1}. The metastable La_2NiO_4 which was formed during heating to 800° C gradually disappears with increasing time. After heating at 800° C for 15 h, the synthesis of the $LaNiO_3$ is completed. At 850° C, the formation of $LaNiO_3$ can be achieved after heating for 2 h. Although the $LaNiO_3$ phase is stably present even after heating at 900° C for 24 h, it obviously decomposes into the $La_4Ni_3O_{10}$, a member of a homologous series of oxides of the general formula $La_{n+1}Ni_nO_{3n+1}$ [14–16], at higher temperatures.

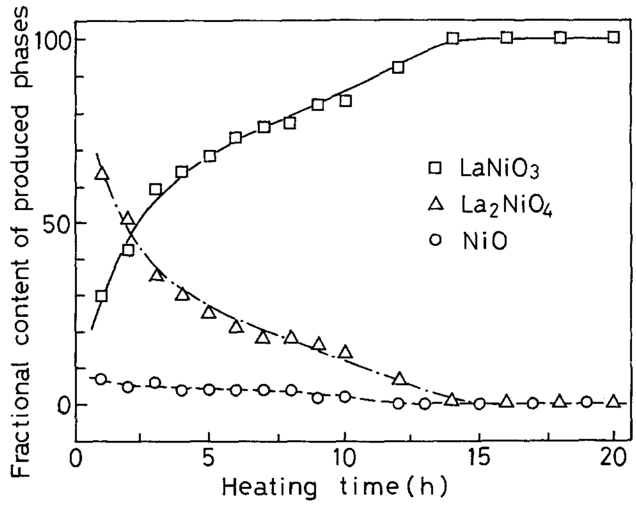

Figure 5 Isothermal formation behaviour of $LaNiO_3$ powder at 800° C.

3.4. Some properties of prepared $LaNiO_3$ powders

Table II shows specific surface areas of the $LaNiO_3$ powders synthesized by heating the mixed metal oxalate coprecipitated under optimum conditions. These values are much higher than those of powders prepared by flux method using Na_2CO_3 [24], and by decomposition of citrate [25] or nitrate [24]. Thus thermal decomposition of the coprecipitated oxalate obtained in the present investigation produces a very fine powder of $LaNiO_3$ having excellent reactivity or catalytic activity. An aggregated powder consisting of those fine particles is clearly seen in a SEM microphotograph of $LaNiO_3$ powder heated at 850° C for 24 h (Fig. 6).

Fractional amounts of Ni^{3+} contained in the synthesized powders are presented in Fig. 7 as a function of heat treatment temperature. In calculating a fraction of Ni^{3+} in the total amount of nickel cations (Ni^{3+} and Ni^{2+}), the molecular formula of the lanthanum nickel oxide powder is assumed to be $LaNiO_{3-\delta}$, because a change in the valency of the nickel cation from Ni^{3+} to Ni^{2+} directly corresponds to the production of oxygen vacancy. Obviously occupation by the divalent nickel ion in the perovskite structure ranges from 0.2 to 0.3 for the powders prepared in the present study. This suggests that the chemical formula of the powders might be $LaNiO_{2.85 \text{ to } 2.90}$. Oxygen vacancies thus formed contribute to ion conductivity in this

TABLE II Specific surface area of prepared $LaNiO_3$ powders

Heating temperature (° C)	Sw (m^2 g^{-1})
800	5.0
850	6.8
900	2.4

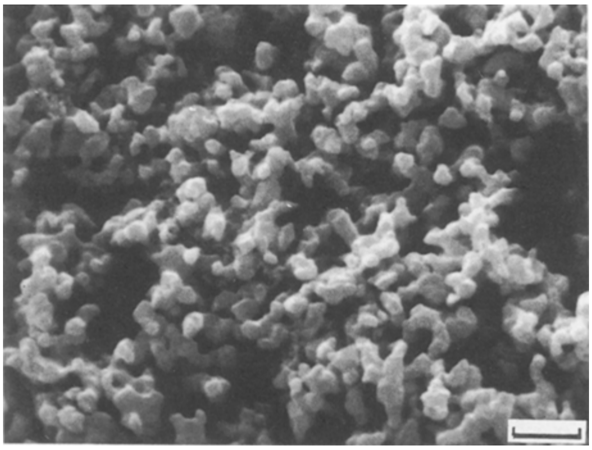

Figure 6 Typical morphology of synthesized $LaNiO_3$ powder (bar = 1 μm).

mixed conductor. A maximum in the Ni^{3+} content seems to be closely related to the structural stability of the perovskite-type $LaNiO_3$. A decreasing content of the Ni^{3+} ion in a powder heated at 900° C is probably due to the partial decomposition of the formed $LaNiO_{3-\delta}$, which can be undetectable by XRD, to some homologous series compound.

4. Conclusions

Coprecipitation of mixed oxalates of lanthanum and nickel cations was examined to prepare a fine powder of $LaNiO_3$ showing superior mixed-conductive property. The results obtained are:

(1) The retarded precipitation of the nickel oxalate is markedly improved by using mixed solutions of distilled water and alcohol as a solvent for an oxalic acid solution, causing a homogeneous deposition of the respective oxalate particles with a required cation ratio.

(2) Detailed examination of some factors affecting the coprecipitation behaviour of the mixed oxalate provides optimum concentration regions for each starting solution and recommended mixing methods.

(3) Heating of the coprecipitated oxalate at 800 to 900° C for 24 h converts the oxalate precursor into a fine, single-phase powder (S_w = 5 to 6 $m^2 g^{-1}$) of the $LaNiO_3$.

(4) Thermal analysis shows that La_2NiO_4 (K_2NiF_4-type high temperature form in the La–Ni–O system) is transiently formed prior to the production of $LaNiO_3$ during thermal decomposition of the coprecipitate.

(5) A quantitative analysis of the mixed valency of the nickel ion in the heat-treated samples suggests that the chemical formula of the powders prepared in the present study might be $LaNiO_{2.85 \text{ to } 2.90}$.

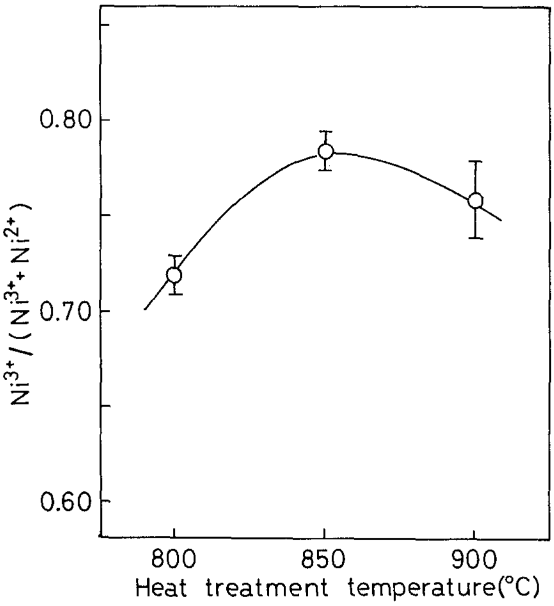

Figure 7 Mixed valency of the nickel ion in prepared $LaNiO_3$ powders.

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