May, 2014

**Comparison of reduction agents
in the synthesis of infinite-layer LaNiO_2 films**

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Abstract

Reduction agents, such as an activated carbon, TiH_2 , and CaH_2 powders, were compared from a viewpoint of the facility for the topotactic reduction of LaNiO_3 to LaNiO_2 films. The activated carbon did not yield infinite-layer LaNiO_2 whereas both of TiH_2 and CaH_2 yielded infinite-layer LaNiO_2 with low resistivity ($\sim 1 \text{ m}\Omega\text{cm}$ at 300 K) as well as metallic behavior down to 70 K. Thermal desorption spectroscopy indicated that H_2 released from metal hydrides plays a dominant role in the topotactic reduction.

PACS: 74.10.+v, 74.62.Dh

Key words: infinite-layer structure, nickel oxide, topotactic reduction, metal hydride

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1. Introduction

In transition-metal oxides, octahedral or tetrahedral oxygen coordination is common as is found typically in perovskites and spinels whereas square-planar coordination is less common. The trend can be understood from the isotropic nature in ionic bonding of oxides. From the simple viewpoint of the crystal field stabilization energy in ionically bonded structures, the square-planar geometry is stabilized by the Jahn-Teller effect, hence it may occur with d^9 and low-spin d^8 (possibly also low-spin d^7) ions [1]. Indeed this seems to be the case for the square-planar oxides formed with Cu^{2+} ($3d^9$), Pd^{2+} ($4d^8$), and Pt^{2+} ($5d^8$) ions [2]. Ni^{1+} , which has the same $3d^9$ electron configuration as Cu^{2+} , may be another candidate to have square-planar coordination. In general, however, nickelates unlike cuprates prefer the octahedral coordination, so it had been believed for a long time that square-planar nickelates *would* not be stable. However, Crespin *et al.* achieved the synthesis of square-planar LaNiO_2 in 1983 [3,4]. They synthesized highly metastable LaNiO_2 by topotactic hydrogen reduction of perovskite LaNiO_3 at low temperatures ($\sim 300^\circ\text{C}$). Here “topotaxy” means that the cation framework is reserved with oxygen atoms removed regularly (not randomly). LaNiO_2 takes the so-called infinite-layer structure, which attracted much interest after the discovery of high- T_c cuprates because it is isostructural to SrCuO_2 , the parent compound of superconducting $\text{Sr}_{0.9}\text{La}_{0.1}\text{CuO}_2$ with $T_c = 44$ K.

After the first synthesis of LaNiO_2 , there were some struggles by other groups to reproduce the experiments by Crespin *et al.* by means of hydrogen reduction, which may be attributed partly to insufficient purity of hydrogen. In 1999, however, Hayward *et al.* succeeded in isolating LaNiO_2 using NaH , one of the most powerful reducing agents [5]. Later, other groups have employed a more convenient hydride,

CaH₂, for the synthesis of infinite-layer LaNiO₂ [6,7]. In our previous articles, we have demonstrated that the thin-film synthesis of LaNiO₂ is rather easy as compared with the bulk synthesis, thanks to a large-surface-to-volume ratio. Our extensive optimizations for synthesis (metal organic decomposition) and subsequent hydrogen reduction conditions have produced conducting LaNiO₂ films with resistivity lower than 1 mΩcm at 300 K [8]. In this article, we report a further improvement in conductivity of LaNiO₂, which is achieved employing metal hydrides as a reducing agent such as TiH₂ and CaH₂. The films show metallic resistivity down to 70 K and a weak upturn at lower temperatures.

2. Experimental

Starting LaNiO₃ films were prepared by metal organic decomposition (MOD) using La and Ni 2-ethylhexanoate solutions. The stoichiometric mixture of 2-ethylhexanoate solutions was spin-coated on (110) NdGaO₃ (NGO) substrates. The films were first calcined at 500°C in air to obtain precursors, next fired at 900°C in a tubular furnace under oxygen ($p_{\text{O}_2} = 1$ atm), and then furnace-cooled in pure oxygen down to 300°C. Subsequently the films were given topotactic reduction with various reducing agents such as activated carbon, TiH₂, and CaH₂. In the reduction, an as-grown LaNiO₃ film was embedded in the powder of the agent in a quartz tube, and then the tube was evacuated ($\leq 10^{-6}$ Torr) and sealed. The sealed tube was heated in a tubular furnace or by a mantle heater. The process parameters in reduction are the temperature (T_{red}) and time (t_{red}). Thermal desorption spectroscopy of H₂ from metal hydrides (without films) was performed using a quadrupole mass spectrometer (Stanford Research Systems, RGA100).

After reduction, the film surface was washed with 2-butanol to remove byproducts and unreacted reducing agents. The film thickness was typically 800 Å although it may vary film by film to some extent. Films with no reduction are referred to “as-grown” in this article. The crystal structure and lattice parameters of the films were determined by a standard $2\theta/\omega$ X-ray diffractometer (XRD) (Rigaku, Smart Lab). The resistivity was measured by a standard four -probe method.

3. Results and discussion

3. 1. Reduction using activated carbon powder

We first present the results using activated carbon powder as a reducing agent. An as-grown LaNiO_3 film was embedded typically in a ~0.2 g amount of activated carbon powder and heated in vacuum at $T_{\text{red}} = 500\text{-}700^\circ\text{C}$ for t_{red} of 30 min. No change in films was observed at $T_{\text{red}} \leq 500^\circ\text{C}$. The films were converted partly to brownmillerite $\text{La}_2\text{Ni}_2\text{O}_5$ by reduction at 600°C , and decomposed completely to La_2NiO_4 at 700°C . Infinite-layer LaNiO_2 is not formed at any T_{red} . The standard reaction enthalpy (ΔH°) for $\text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$ is -393.5 kJ/mol, which is smaller in magnitude than -483.6 kJ/mol for $2\text{H}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{H}_2\text{O(g)}$ [9]. But this may not be a reason for the unsuccessful result. The true reason may be that reduction of LaNiO_3 films with carbon powder proceeds via solid-solid reaction, which requires higher temperatures than reduction via solid-gas reaction. In fact, the topotactic reduction of LaNiO_3 films to LaNiO_2 in hydrogen gas is completed at $380\text{-}420^\circ\text{C}$ for 10 min, and the decomposition to La_2NiO_4 starts at $T_{\text{red}} \geq 450^\circ\text{C}$, indicating that the reduction proceeds at substantially lower temperatures than in reduction with carbon. The solid-state reaction route appears not to be favorable for stabilizing infinite-layer

LaNiO₂.

3. 2. Thermal desorption spectroscopy for TiH₂ and CaH₂

So far NaH and CaH₂ have been employed as a reducing agent for the topotactic reduction from LaNiO₃ to LaNiO₂. But TiH₂ has not been attempted previously as far as we know. There is some controversy regarding how the reduction of oxides proceeds with hydrides, namely via solid-solid (oxide-hydride) reaction or via H₂ gas released from hydrides. The first report by Hayward *et al.* supported the solid-solid reaction since intimate grinding of LaNiO₃ and NaH powders is inevitable for the successful synthesis of LaNiO₂. In contrast, the recent report by Kobayashi *et al.* supported the reaction via H₂ gas from the following experimental observations [10]. Employing films of LaNiO₃ instead of powder, they performed reduction with a film and CaH₂ either physically contacted or separated, and compared the results. LaNiO₂ was obtained even in separated reduction at the same temperature (280°C) as in contacted reduction, but with a longer time required. This is strong evidence that the reduction proceeds via gas phase intermediates, most likely H₂ gas. In order to evaluate the partial pressure of H₂ gas released from metal hydrides in reduction, we performed thermal desorption spectroscopy. Figure 1 shows the results. It plots the partial hydrogen pressure (p_{H_2}) released from CaH₂ and TiH₂ as a function of temperature on ramping up the temperature by 1.6°C/min. For TiH₂, p_{H_2} starts to rise at ~150°C, and monotonically increases with temperature. After a rapid increase at 380~400°C, p_{H_2} becomes nearly constant upon a further increase of temperature. The reaction for releasing H₂ gas from TiH₂ appears to be simply $\text{TiH}_2 \rightarrow \text{Ti(s)} + \text{H}_2(\text{g})$. In contrast, for CaH₂, p_{H_2} shows strange behavior. Namely, p_{H_2} is already high at ambient

temperature, and the p_{H_2} - T curve is shifted to lower temperatures by 120-150°C as compared with the p_{H_2} - T curve for TiH_2 up to 250°C. The p_{H_2} - T of CaH_2 flattens above 250°C and drops by one order of magnitude with some wiggles above 300°C. The irregular behavior observed seems to indicate that the reaction to release H_2 in CaH_2 may not be simply $\text{CaH}_2 \rightarrow \text{Ca(s)} + \text{H}_2(\text{g})$. This speculation is also supported from the rather high dissociation temperature (885°C) reported for CaH_2 [11]. Kobayashi *et al.* pointed out the same issue [10]. According to their estimate, the equilibrium constant for $\text{CaH}_2 \rightarrow \text{Ca(s)} + \text{H}_2(\text{g})$ is only 10^{-8} even at 400°C. The value makes it difficult to explain the observed high p_{H_2} at temperatures below 400°C. Instead of the simple dissociation, Kobayashi *et al.* proposed the reaction between the hydride and hydroxide, namely $\text{CaH}_2 + \text{Ca(OH)}_2 \rightarrow 2\text{CaO(s)} + 2\text{H}_2(\text{g})$. The equilibrium constant of this reaction is estimated to be high (10^{12} at 400°C). Ca(OH)_2 is always present in CaH_2 powder as impurity, which is produced by the reaction between CaH_2 and atmospheric moisture. This reaction may explain the observed irregular p_{H_2} - T curve [12].

3. 3. Reduction using TiH_2

We next present the experimental results of reduction using TiH_2 . The films were reduced at different T_{red} (250-400°C) with a fixed t_{red} of 120 min. In reduction using TiH_2 , the amount of TiH_2 is also one important parameter, so it was varied from ~0.5 g to ~25 g. With 0.5 g of TiH_2 , the reduction at $T_{\text{red}} = 350^\circ\text{C}$ yielded films of a mixture of $\text{La}_2\text{Ni}_2\text{O}_5$ and LaNiO_2 whereas the reduction at $T_{\text{red}} = 375^\circ\text{C}$ yielded films of single-phase LaNiO_2 . The reduction at $T_{\text{red}} \geq 400^\circ\text{C}$ decomposed the infinite-layer phase completely and yielded films of La_2NiO_4 . The range of T_{red} for single-phase

LaNiO₂ films to form is very narrow and it is close to the temperature range (350-400°C) in which p_{H_2} from TiH₂ rapidly increases as shown in Fig. 1. The optimum T_{red} varies with the amount of TiH₂ in reduction. Figure 2 summarizes the (002) peak intensity and the c_0 of infinite-layer LaNiO₂ as a function of T_{red} . As the amount of TiH₂ increases, the optimum T_{red} becomes lower ($T_{\text{red}} = 375^\circ\text{C}$ for 0.5 g, 320°C for 5 g, and 288°C for 25 g), and simultaneously the (002) peak intensity of the films reduced at optimum T_{red} becomes stronger. As seen in Fig. 2(b), our c_0 values of the films reduced using TiH₂ is in a fair agreement with the c_0 of bulk samples. The c_0 values decreases slightly with T_{red} as a global trend on comparing several LaNiO₂ films reduced with a different amount of TiH₂.

Figure 3 shows the temperature dependence of resistivity (ρ - T) for the LaNiO₂ films prepared with a different amount of TiH₂. The films were reduced so as to minimize the resistivity. The T_{red} is 375°C for 0.5 g, 325°C for 5 g, and 300°C for 25 g, respectively, which is almost the same as or slightly (5-10°C) higher than the T_{red} giving the strongest XRD peaks. All the films in Fig. 3 are metallic down to 70-110 K but with a resistivity upturn at lower temperatures. The $\rho(300\text{ K})$ is $\sim 1\text{ m}\Omega\text{cm}$ for the films reduced with 5 g and 25 g of TiH₂ whereas it is $\sim 3.4\text{ m}\Omega\text{cm}$ for the film reduced with 0.5 g of TiH₂. Summarizing the results with TiH₂, a larger amount ($\geq 5\text{ g}$) of TiH₂ lowers the reduction temperature, and yields LaNiO₂ films with better crystallinity and lower resistivity.

3. 4. Reduction using CaH₂

In reduction using CaH₂, the amount of CaH₂ is fixed ($\sim 0.5\text{ g}$) since a larger amount of CaH₂ made the results worse. The T_{red} was varied from 275 to 400°C and

the t_{red} was fixed at 120 min. The reduction at $T_{\text{red}} = 275^\circ\text{C}$ yielded films of a mixture of starting LaNiO_3 , $\text{La}_2\text{Ni}_2\text{O}_5$, and LaNiO_2 whereas the reduction at $T_{\text{red}} = 300\text{-}375^\circ\text{C}$ yielded single-phase LaNiO_2 films. The reduction at $T_{\text{red}} \geq 400^\circ\text{C}$ decomposed the infinite-layer phase and yielded films of La_2NiO_4 . The (002) peak intensity and the c_0 of infinite-layer LaNiO_2 as a function of T_{red} is summarized in Fig. 2. As seen in Fig. 2(a), the range of T_{red} for single-phase LaNiO_2 to form in CaH_2 reduction is wide and covers the ranges of T_{red} for single-phase LaNiO_2 to form in the reduction with 0.5, 5, and 25 g of TiH_2 . As shown in Fig. 2, the XRD peaks intensity grows with lowering T_{red} . This trend is also seen in TiH_2 reduction if one compares the peak intensities for a different amount of TiH_2 . Figure 4 shows the ρ - T curves for the LaNiO_2 films reduced with CaH_2 at different T_{red} ($300\text{-}375^\circ\text{C}$). The films reduced at $T_{\text{red}} = 300^\circ\text{C}$ and 325°C show $\rho(300\text{ K})$ as low as $\sim 1\text{ m}\Omega\text{cm}$ and a metallic temperature dependence down to 70 K but with an upturn at lower temperatures. Increasing T_{red} , the $\rho(300\text{ K})$ and also the resistivity minimum temperature (T_{min}) become higher. The trend in Fig. 4 resembles the trend seen in the ρ - T (Fig. 3) of the films reduced with the different amount of TiH_2 . This implies that the trend in Fig. 3 may also be due to the increase of T_{red} accompanied with a reduced amount of TiH_2 in reduction.

3.5. Comparison of TiH_2 , CaH_2 , and H_2 reduction

Next we compare the properties of LaNiO_2 films prepared by different reduction agents. Figure 5 is a summary of the results for our best LaNiO_2 films prepared with TiH_2 and CaH_2 : (a) XRD and (b) ρ - T . For comparison, the data for films reduced with flowing hydrogen gas ($p_{\text{H}_2} = 1\text{ atm}$) are also included. For each reduction agent, the reduction conditions are optimized. In Fig. 5(a), the c_0 of the

LaNiO₂ films are also included. The values hardly depend on the reduction agents. The difference by reduction agents is observed most prominently in the resistivity. The LaNiO₂ films prepared by either TiH₂ or CaH₂ reduction show lower $\rho(300\text{ K})$ and lower $T_{\min}$ than the films prepared by H₂ reduction. The $T_{\min}$ is 70 K in metal-hydride reduction whereas it is 260 K in hydrogen reduction. One may think that the difference arises from the difference in the reduction process. For example, direct solid-solid (oxide-hydride) reaction may play an important role in metal-hydride reduction. But we argue against this possibility from the following reasons. Firstly, the infinite-layer phase did not form when we heated up a film embedded in metal-hydride powder in dynamic vacuum, namely we kept pumping a quartz tube left unsealed by a diffusion pump (base pressure of $\sim 10^{-6}$ Torr) during TiH₂/CaH₂ reduction. In dynamic vacuum, H₂ gas released from metal hydrides is pumped out and the reduction route via gas-solid reaction is cut off. The experimental results strongly supports that the gas phase is prerequisite for the formation of LaNiO₂. Secondly there is not much difference in the T_{red} between TiH₂/CaH₂ and H₂ reduction, as can be seen in the summary in Table I.

We speculate the reason for the difference in the resistivity of the films prepared by TiH₂/CaH₂ and H₂ reduction as follows. As shown in fig. 5(a), all the films are infinite-layer single-phase but a mixture of *a*- and *c*-axis oriented grains. The (200) peak of *a*-axis grains is smaller in the films reduced by metal hydrides than in the films reduced by flowing hydrogen gas, although the reason is yet to be understood. The smaller amount of *a*-axis oriented grains is favorable for conductivity if one assumes that the electron transport takes place in the two-dimensional NiO₂ planes. As another reason, the hydrogen gas we used for reduction was not of an ultra-pure

semiconductor grade but of a standard grade, and may contain O₂, H₂O, CO₂, etc. as impurities. Therefore the environment during reduction may be cleaner in metal-hydride reduction than in hydrogen reduction. This may be a possible reason why short t_{red} (~10 min) is favorable in hydrogen reduction whereas long t_{red} (2 -12 hr) is favorable in metal hydride reduction.

4. Summary

In summary, activated carbon, CaH₂, and TiH₂ were examined from a viewpoint of the suitability for topotactic reduction to isolate infinite-layer LaNiO₂ from LaNiO₃ films. In metal-hydride reduction, the gas-solid reduction proceeds with hydrogen released from the thermal decomposition of TiH₂ or from the reaction between CaH₂ and Ca(OH)₂, which is effective to isolate LaNiO₂ at low temperatures. The low resistivity with $\rho(300\text{ K}) \sim 1\text{ m}\Omega\text{cm}$ as well as the metallic resistivity down to 70 K are observed in the LaNiO₂ films prepared with either TiH₂ or CaH₂. By contrast, no LaNiO₂ film has been obtained with an activated carbon. This implies that the solid-state reduction is not favorable for low-temperature reduction.

Acknowledgements

The work was partly supported by KAKENHI B (23340098) from Japan Society for the Promotion of Science (JSPS) and also by Advanced Low Carbon Technology (ALCA), Japan Science and Technology Agency.

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Table I. Summary of the optimal reduction temperature T_{red} with a fixed t_{red} for various reduction agents.

Reduction agents	amount	Reduction time (t_{red})		
		10 min	2 h	12 h
CaH ₂	0.5 g	375°C	300°C	275°C
TiH ₂	0.5 g	425°C	375°C	325°C
	5 g		325°C	
	25 g		300°C	
H ₂	1 atm	380°C	360°C *	

*This value of T_{red} in H₂ reduction is not for t_{red} of 2 h but of 1.5 h.

Figure caption

Figure 1. Partial hydrogen pressures (p_{H_2}) taken for 0.5g of TiH_2 and CaH_2 of on ramping up the temperature to 450°C by 1.6°C/min in vacuum ($\sim 10^{-6}$ Torr).

Figure 2. (a) The (002) peak intensity and (b) c -axis length of $LaNiO_2$ films prepared with CaH_2 and TiH_2 as a function of T_{red} , respectively. In fig. 2(b), the c_0 of bulk samples is also included by the thick bar, where $c_0 = 3.376$ Å for hydrogen reduced samples [3] and $c_0 = 3.375$ Å for NaH reduced samples [5].

Figure 3. The temperature dependence of resistivity ρ - T for $LaNiO_2$ films reduced with a different amount of TiH_2 (0.5-25 g).

Figure 4. ρ - T characteristics of $LaNiO_2$ films reduced with CaH_2 at various T_{red} (300-375°C).

Figure 5. Structural and transport data for $LaNiO_2$ films prepared with various reduction agents after optimizing reduction conditions: (a) XRD patterns and (b) ρ - T . For comparison, the data for films reduced in hydrogen is also included. The reduction conditions of these films are as follows: $T_{red} = 325^\circ\text{C}$ and $t_{red} = 2$ h in reduction with TiH_2 (5 g), $T_{red} = 300^\circ\text{C}$ and $t_{red} = 2$ h in reduction with CaH_2 (0.5 g), , $T_{red} = 380^\circ\text{C}$ and $t_{red} = 10$ min in hydrogen reduction ($p_{H_2} = 1$ atm).

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5