



Comparison of reduction agents in the synthesis of infinite-layer LaNiO₂ films



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ABSTRACT

Reduction agents, such as activated carbon, TiH₂, and CaH₂, were compared from a viewpoint of the facility for the topotactic reduction of LaNiO₃ to LaNiO₂ films. Activated carbon did not yield infinite-layer LaNiO₂ whereas both of TiH₂ and CaH₂ yielded infinite-layer LaNiO₂ with low resistivity (~ 1 m Ω cm at 300 K) as well as metallic behavior down to 70 K. Thermal desorption spectroscopy indicated that H₂ released from metal hydrides plays a dominant role in the topotactic reduction.

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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 Cu²⁺ ($3d^9$), Pd²⁺ ($4d^8$), and Pt²⁺ ($5d^8$) ions [2]. Ni¹⁺, which has the same $3d^9$ electron configuration as Cu²⁺, 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 LaNiO₂ in 1983 [3,4]. They synthesized highly metastable LaNiO₂ by topotactic hydrogen reduction of perovskite LaNiO₃ at low temperatures (~ 300 °C). Here “topotaxy” means that the cation framework is reserved with oxygen atoms removed regularly (not randomly). LaNiO₂ is crystallized in the so-called infinite-layer structure, which attracted much interest after the discovery of high- T_c cuprates because it is isostructural to SrCuO₂,

the parent compound of superconducting Sr_{0.9}La_{0.1}CuO₂ with $T_c = 44$ K.

After the first synthesis of LaNiO₂, 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 LaNiO₂ 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 m Ω cm 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 (1 1 0) 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 ($p_{O_2} = 1$ atm), and then furnace-cooled in

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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 LaNiO₃ film was embedded typically in a ~ 0.2 g amount of activated carbon powder and heated in vacuum at $T_{\text{red}} = 500\text{--}700$ °C for t_{red} of 30 min. No change in films was observed at $T_{\text{red}} \leq 500$ °C. The films were converted partly to brownmillerite La₂Ni₂O₅ by reduction at 600 °C, and decomposed completely to La₂NiO₄ at 700 °C. Infinite-layer LaNiO₂ was not formed at any T_{red} . The standard reaction enthalpy (ΔH°) for C(s) + O₂(g) → CO₂(g) is -393.5 kJ/mol, which is smaller in magnitude than -483.6 kJ/mol for 2H₂(g) + O₂(g) → 2H₂O(g) [9]. But this may not be a reason for the unsuccessful result. The true reason may be that reduction of LaNiO₃ 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 LaNiO₃ films to LaNiO₂ in hydrogen gas is completed at 380–420 °C for 10 min, and the decomposition to La₂NiO₄ starts at $T_{\text{red}} \geq 450$ °C, indicating that the reduction with hydrogen gas proceeds at substantially lower temperatures than the 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. Fig. 1 shows the

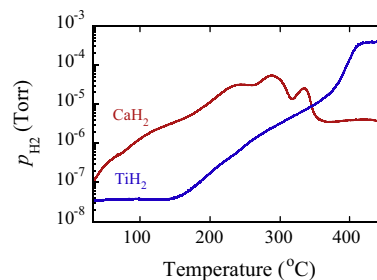


Fig. 1. Partial hydrogen pressures (p_{H_2}) taken for 0.5 g of TiH₂ and CaH₂ of on ramping up the temperature to 450 °C by 1.6 °C/min in vacuum ($\sim 10^{-6}$ Torr).

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 TiH₂ → Ti(s) + H₂(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 TiH₂ up to 250 °C. The p_{H_2} – T of CaH₂ 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 H₂ in CaH₂ may not be simply CaH₂ → Ca(s) + H₂(g). This speculation is also supported from the rather high dissociation temperature (885 °C) reported for CaH₂ [11]. Kobayashi et al. pointed out the same issue [10]. According to their estimate, the equilibrium constant for CaH₂ → Ca(s) + H₂(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 CaH₂ + Ca(OH)₂ → 2CaO(s) + 2H₂(g). The equilibrium constant of this reaction is estimated to be high (10^{12} at 400 °C). Ca(OH)₂ is always present in CaH₂ powder as impurity, which is produced by the reaction between CaH₂ and atmospheric moisture. This reaction may explain the observed irregular p_{H_2} – T curve [12].

3.3. Reduction using TiH₂

We next present the experimental results of reduction using TiH₂. The films were reduced at different T_{red} (250–400 °C) with a fixed t_{red} of 120 min. In reduction using TiH₂, the amount of TiH₂ is also an important parameter, so it was varied from ~ 0.5 g to ~ 25 g. With 0.5 g of TiH₂, the reduction at $T_{\text{red}} = 350$ °C yielded films of a mixture of La₂Ni₂O₅ and LaNiO₂ whereas the reduction at $T_{\text{red}} = 375$ °C yielded films of single-phase LaNiO₂. The reduction at $T_{\text{red}} \geq 400$ °C decomposed the infinite-layer phase completely and yielded films of La₂NiO₄. 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. Fig. 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 ($T_{\text{red}} = 375$ °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

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