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Low-temperature synthesis of the infinite-layer compound $LaNiO_2$ using CaH_2 as reductant

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ABSTRACT

We have successfully synthesized *bulk* samples of the infinite-layer compound $LaNiO_2$ by reduction of the perovskite $LaNiO_3$ using CaH_2. First, $LaNiO_3$ has been prepared using molten KOH at 450 °C. Next, the infinite-layer compound $LaNiO_2$ has been synthesized by heating $LaNiO_3$ mixed with a double stoichiometric excess of CaH_2 in an evacuated Pyrex tube at 300 °C for 24 h.

1. Introduction

The compound $LaNiO_2$ with formally monovalent Ni-ions synthesized first by Crespin et al. [1] has attracted great interest, because it is isostructural to the so-called infinite-layer compound $SrCuO_2$ which is a parent material of high-T_c superconducting cuprates, as shown in Fig. 1. Moreover, the $3d^9$ electronic configuration of Ni^+ is the same as that of Cu^{2+} in the high-T_c cuprates. Accordingly, $LaNiO_2$ is a promising candidate for a parent material of new high-T_c superconductors. The synthesis of $LaNiO_2$ by Crespin et al. [1] was done by topotactic reduction of the perovskite $LaNiO_3$ using H_2 at 250–450 °C, but, it was hard to synthesize it reproducibly. Later, the reproducible synthesis of $LaNiO_2$ was achieved by Hayward et al. [2] through oxygen deintercalation from $LaNiO_3$ using NaH as reductant in a narrow temperature range of 190–210 °C, which was limited by the low decomposition-temperature of NaH (210 °C).

Recently, an infinite-layer compound $SrFeO_2$ has been synthesized by low-temperature reduction of the perovskite $SrFeO_3$ using CaH_2 at 280 °C by Tsujimoto et al. [3]. Since CaH_2 has a high decomposition-temperature (885 °C) and is relatively stable, it is easier to handle CaH_2 than NaH. In addition, very recently, both Kawai et al. and Kaneko et al. have successfully synthesized a thin film of $LaNiO_2$ by low-temperature reduction using CaH_2 and H_2, respectively [4,5].

In this paper, we report the synthesis of *bulk* samples of the infinite-layer compound $LaNiO_2$ by low-temperature reduction of $LaNiO_3$ using CaH_2. Here, we have prepared the parent compound $LaNiO_3$ by the method using molten KOH, which is useful for the preparation of compounds containing transition metals in the elevated oxidation state, and is much easier than the sol–gel and coprecipitation methods used by Crespin et al. [1] and Hayward et al. [2], respectively.

2. Experimental

Polycrystalline *bulk* samples of $LaNiO_2$ were synthesized as follows. First, powdered samples of $LaNiO_3$ with the perovskite structure were prepared using molten KOH. KOH of 50 g was placed in an alumina crucible and melted at 450 °C in air. After 6.5 h, a mixture of La_2O_3 of 0.3428 g and NiO of 0.1572 g (La:Ni = 1:1 in molar ratio) was added. The crucible was kept at 450 °C for 6 h and then cooled to room temperature. Black polycrystalline powder was isolated by dissolving the hydroxides with distilled water and dried at 130 °C in air [6]. Next, the reduction of $LaNiO_3$ was performed using CaH_2 as reductant. The obtained powder of $LaNiO_3$ was mixed with a double stoichiometric excess of CaH_2, ground finely and then pressed into pellets in an Ar-filled glove box. Then, the pellets were sealed in an evacuated Pyrex tube and then heated at 150–400 °C for 24 h. The products were washed with NH_4Cl in anhydrous ethanol to remove the residual CaH_2 and the reaction byproduct CaO. All products were characterized by powder X-ray diffraction using Cu Kα radiation at room temperature.

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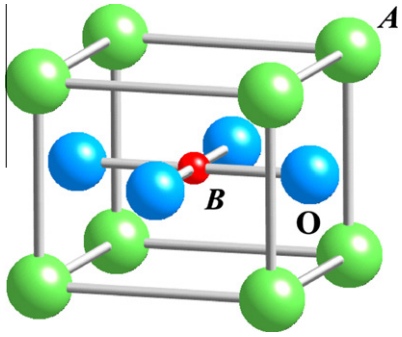

Fig. 1. Crystal structure of the infinite-layer compound ABO_2.

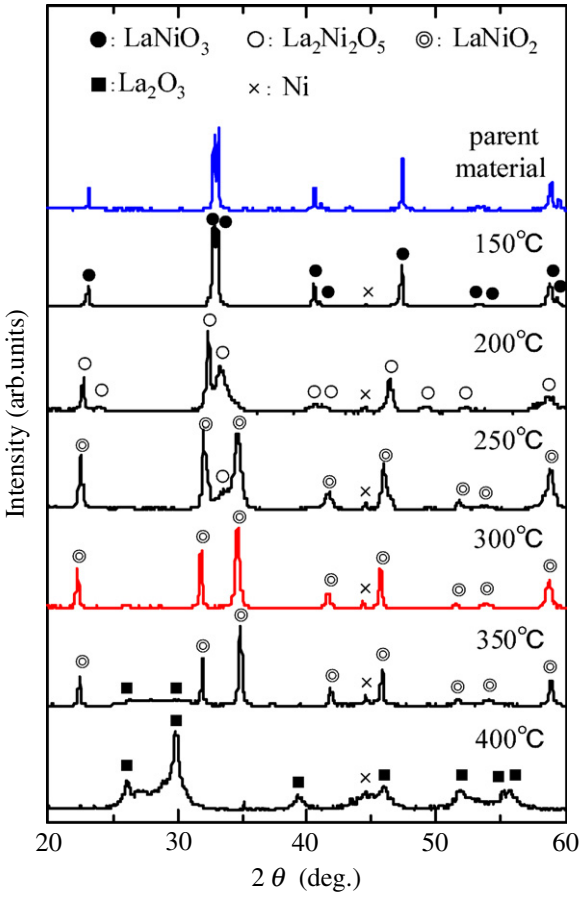

Fig. 2. Powder X-ray diffraction patterns of products obtained by the reaction between $LaNiO_3$ and CaH_2 at various reaction-temperatures using Cu Kα radiation.

3. Results

Fig. 2 shows the variation of the powder X-ray diffraction patterns with the heat-treatment-temperature for the products obtained by the reaction between $LaNiO_3$ and CaH_2. $LaNiO_3$ has not reacted with CaH_2 at 150 °C. At 200 °C, $La_2Ni_2O_5$ with Ni^{2+} is formed. The infinite-layer compound $LaNiO_2$ with Ni^{+} is dominant at 250 °C, though a small amount of $La_2Ni_2O_5$ still remains. An almost single-phase sample of $LaNiO_2$ is obtained at 300 °C, though a very small amount of Ni is included. The lattice parameters of $LaNiO_2$ are estimated to be $a = 3.964$ Å and $c = 3.399$ Å, which are in good agreement with those in the previous reports [1,2]. At 350 °C, $LaNiO_2$ is dominant, but $LaNiO_3$ is partially decomposed into La_2O_3 and Ni. Then, $LaNiO_3$ is completely decomposed to La_2O_3 and Ni at high temperatures above 400 °C.

4. Conclusions

We have successfully synthesized *bulk* samples of the infinite-layer compound $LaNiO_2$. First, the pervskite $LaNiO_3$ was prepared using molten KOH at 450 °C. Next, $LaNiO_2$ was synthesized by reduction of $LaNiO_3$ with CaH_2 as reductant at 300 °C. At present, unfortunately, we have not yet succeeded in elucidating intrinsic magnetic properties of $LaNiO_2$ because of the inclusion of a small amount of ferromagnetic Ni in the samples.

Acknowledgments

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