

Hydrothermal synthesis of non-stoichiometric Co–Ga oxide nanoparticles

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We synthesized non-stoichiometric Co–Ga nanoparticles with controllable Co/Ga molar ratio by using supercritical hydrothermal synthesis. By applying X-ray absorption fine structure analysis at Co K-edge, non-stoichiometric Co–Ga NPs were found to have large numbers of cobalt atoms occupying octahedral sites compared to CoGa_2O_4 . Owing to the high octahedral occupancy, their superparamagnetic behavior at room temperature was observed for the first time.

1 Introduction

Mixed metal oxides with a spinel-type crystal structure (Fig. 1) have attracted considerable interest owing to their remarkable electrical, optical, magnetic, and catalytic properties. Spinel-type Ga-based metal oxide, CoGa_2O_4 has been considered for applications in ceramic pigments, electrocatalysts, and cathodes and anodes for various types of capacitors.

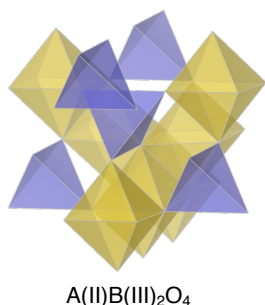


Fig. 1: Crystal structure of spinel-type metal oxides [1].

Material properties of the spinel compounds could be further enhanced by producing their counterpart with nonstoichiometric composition and nanosize. However, trials on the production of non-stoichiometric spinel-type cobalt gallate nanoparticles (Co–Ga NPs) and studies on their properties have been rarely studied.

In this work, we report the supercritical hydrothermal synthesis of Co–Ga NPs at 400 °C for 10 min without performing the calcination process. Spinel-type Co–Ga NPs with broad range of Co/Ga molar ratios were synthesized by controlling the pH value of the precursor solutions. By applying X-ray absorption fine structure (XAFS) analysis at Co K-edge, products were found to have large octahedral cobalt occupancy compared to calcined CoGa_2O_4 , and this resulted in a new magnetic behavior at room temperature.

2 Experiment

Preparation of Co–Ga NPs. The batch-type supercritical hydrothermal synthesis was conducted as shown in Fig. 2. The precursor solution was prepared by dissolving cobalt (II) nitrate hexahydrate and gallium (III) nitrate n-hydrate with a concentration of 0.050 mol/L and 0.10 mol/L, respectively (Co/Ga = 0.5) in pure water (2.0 mL). To this aqueous solution, 1.0 mol/L NaOH solution were added to adjust pH to 7, 9, and 11. The precursor solutions including solid precipitates (1.5 mL) were then transferred to a pressure-resistant Hastelloy reactor (inner volume of 5.0 mL) and put in a furnace with constant temperature of 400 °C. The reactor was taken out after 10 min. The reaction was terminated by submerging the reactor into a cold-water bath. Solid and liquid products were collected and separated for further analysis.

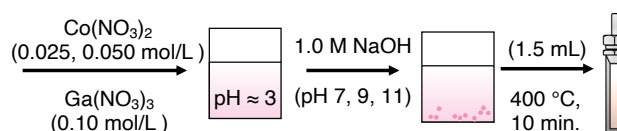


Fig. 2: Experimental procedure.

After centrifugation and decantation, the solid products were analyzed by X-ray diffraction (XRD), transmission electron microscopy (TEM), and inductively coupled plasma atomic emission spectroscopy (ICP-AES) to confirm crystalline phase, morphology and composition (Co/Ga molar ratio) of the products.

XAFS analysis. Ga K-edge and Co K-edge XAFS spectra were measured with the transmission mode at BL-9A, Photon Factory, KEK, Japan. Athena was used for the data processing of the X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analyses [2].

Linear combination of k^3 -weighted $\chi(k)$ oscillation.

Site distribution of cobalt atoms of the products was determined by using EXAFS data. To determine Co occupancy at octahedral and tetrahedral sites, a linear combination of k^3 -weighted $\chi(k)$ oscillation of Co–Ga NPs at Co K-edge was conducted for each pH condition while using theoretically calculated k^3 -weighted $\chi(k)$ oscillations of $^{IV}(\text{Co})^{VI}[\text{Ga}_2]\text{O}_4$ and $^{IV}(\text{Ga})^{VI}[\text{CoGa}]\text{O}_4$ [3]. This calculation was enlightened by the concept reported by Harada *et al* [4].

Magnetism investigation. Alternating current (AC) and direct current (DC) magnetization measurements were conducted using the magnetic properties measurement system (MPMS-XL; Quantum Design).

3 Results and Discussion

XRD patterns and TEM images showing the crystalline phase and morphology of the solid products are summarized in Fig. 3. The diffraction patterns for products prepared at pH 7–11 were indexed based on an ICSD card (ICSD: 172183) to single-phase spinel-type cobalt gallium metal oxides (CoGa_2O_4) with $Fd-3m$ space group. TEM images are showing synthesized spinel-type cobalt gallate metal oxides were nanoparticles with octahedron morphology. To investigate the composition of the spinel-type Co–Ga NPs, solid products at each pH were dissolved in a mixture of nitric acid and hydrogen peroxide with a volume ratio of 1:1, and Co/Ga molar ratio in the resultant solution was measured by ICP-AES. In this work, the Co/Ga molar ratio was defined as the composition of the products at each pH condition, and was summarized in Fig. 3(b). Co/Ga molar ratios at pH 7–11 were nonstoichiometric composition, and were larger than that in a stoichiometric CoGa_2O_4 prepared

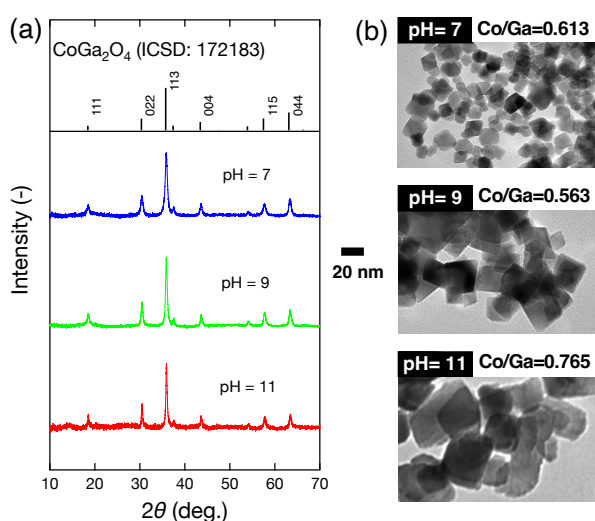


Fig. 3: (a) XRD patterns and (b) TEM images of solid products produced at 400 °C at pH 7–11.

from traditional calcination method (Co/Ga = 0.50). Therefore, prepared spinel-type Co–Ga NPs may have site distributions of metal atoms that have not been realized by the traditional calcination method.

Because there are more cobalt atoms existing in the unit cell of the prepared non-stoichiometric Co–Ga NPs compared to CoGa_2O_4 , we evaluated the site distribution of metal atoms. In detail, the metal occupancy of Co atoms at octahedral and tetrahedral sites for each pH condition was quantitatively evaluated by considering that the measured k^3 -weighted $\chi(k)$ oscillation at the Co K-edge of the products is a linear combination of those of $^{IV}(\text{Co})^{VI}[\text{Ga}_2]\text{O}_4$ (normal spinel) and $^{IV}(\text{Ga})^{VI}[\text{CoGa}]\text{O}_4$ (inverse spinel) [3]. The k^3 -weighted $\chi(k)$ oscillations of the normal spinel and the inverse spinel at the Co K-edge were theoretically calculated by Larch [5], as shown in Fig. 4(a) and Fig. 4(b). Meanwhile, Fig. 4(c) is showing the fitting results. The occupancies of Ga and Co calculated from the previous linear combination of the prepared non-stoichiometric Co–Ga NPs are summarized in Fig. 5. As a result, cobalt atoms are mainly occupying octahedral sites, and extremely surpassed cobalt octahedral occupancy in a calcined CoGa_2O_4 (line with cyan color). Moreover, because Co atoms are the only magnetic metal atoms in the unit cell of spinel-type cobalt gallate metal oxides. Nonstoichiometric Co–Ga NPs prepared in this work with large cobalt octahedral occupancy might exhibit different magnetic behavior compared to CoGa_2O_4 .

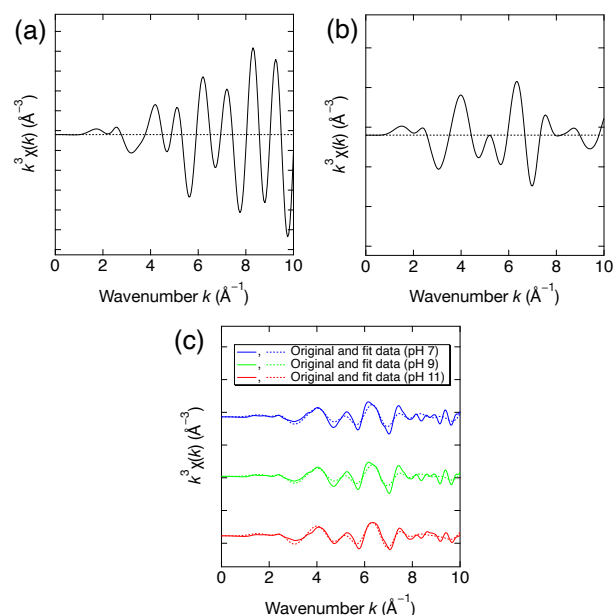


Fig. 4: Theoretically calculated and measured k^3 -weighted $\chi(k)$ oscillation at Co K-edge of (a) $^{IV}(\text{Co})^{VI}[\text{Ga}_2]\text{O}_4$, (b) $^{IV}(\text{Ga})^{VI}[\text{CoGa}]\text{O}_4$, and (c) linear combination fitting results [3].

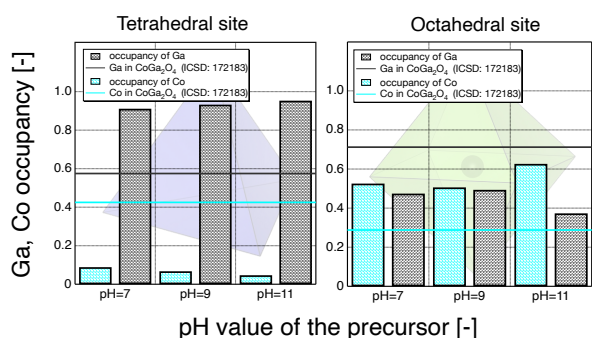


Fig. 5: Site distribution of Ga, Co atoms in tetrahedral and octahedral sites of the unit cell of the spinel-type nonstoichiometric Co-Ga NPs prepared in this work.

The M-H curves of the Co-Ga NPs measured at room temperature are shown in Fig. 6. Notably, the magnetic behavior of our products at room temperature was different from calcined CoGa_2O_4 with stoichiometric composition [6]. The magnetism was considered to be the combination of partially paramagnetic and partially ferromagnetic (superparamagnetic) behaviors. We consider this because the high cobalt octahedral occupancies at pH 7–11 were larger than 0.390 [7], and consequently super-exchange interaction of J_{BB} percolated through the nanocrystal. In this way, a magnetic domain develops macroscopically in the crystals and ferromagnetism was induced. In summary, superparamagnetic behavior of spinel-type Co-Ga NPs at room temperature was observed for the first time with the help of non-stoichiometry and nanosizing in the present technique.

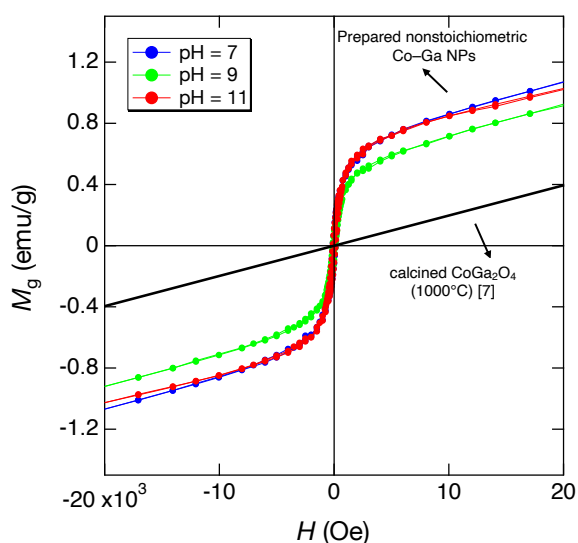


Fig. 6: M-H curves (measured at 300 K) of non-stoichiometric Co-Ga NPs produced at 400 °C using precursor solutions with pH 7–11.

Acknowledgement

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References

- [1] K. Momma and F. Izumi, *J. Appl. Cryst.* **44**, 1272 (2011).
- [2] B. Ravel and M. Newville, *J. Synchrotron Radiat.* **12**, 537 (2005).
- [3] B. Xie, C. Numako, T. Naka, S. Takami, *Cryst. Growth Des.* **23**, 2511 (2023).
- [4] M. Harada, M. Kuwa, R. Sato, T. Teranishi, S. Maenosono, S., *ACS Appl. Nano Mater.* **3**, 8389 (2020).
- [5] M. Newville and M. Larch, *J. Phys.: Conf. Ser.* **430**, 012007 (2013).
- [6] S. Mathur, C. Cavelius, H. Shen, *Z. Anorg. Allg. Chem.* **635**, 2106 (2009).
- [7] F. Scholl and K. Binder, *Z. Phys. B - Condens. Matter* **39**, 239 (1980).

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