Fabrication of $SmCo_x$ Nanoparticles as a Potential Candidate of Materials for Super-high-density Magnetic Memory: Use of Gold as the Third Element

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The $SmCo_5$ magnetic nanoparticles were prepared via simultaneous reduction of $Sm(acac)_3 \cdot xH_2O$, $Co(acac)_3$, and AuCl in tetraethylene glycol (TEG) in the presence of stabilizing agents. The presence of Au is considered to promote the formation of $SmCo_x$ ($x = 5$–8.5) nanoparticles. As-prepared $SmCo_x$ nanoparticles had an average diameter of 6.9 nm and a structure similar to $CaCu_5$ crystal. Magnetic measurements of these particles exhibited a coercivity (H_c) of 1500 Oe at 300 K.

Among metal nanoparticles,[1] nanomagnets have received much attention because of their potential application to super-high-density magnetic memories, which are strongly required by recent rapid development of information technology. The report by Sun et al. in 2000[2] has provided a strong shock to researchers in the field of information technology, especially the super-high-density magnetic memory. Many studies have started after his report.[2] Among them, direct fabrication of fct-structured FePt nanoparticles by a polyol process has been conducted recently.[3–5] Here, we have paid attention not to FePt magnet, but a rare-earth permanent magnet, which has much higher coercivity and less cost than FePt magnet[6] and is practically used as a small magnet in the bulk state. Among rare-earth permanent magnets, $SmCo_5$ with a $CaCu_5$ structure has the highest corecivity.[7,8] Thus, $SmCo_5$ nanoparticles are expected as a potential candidate for nanomagnet with specific magnetic properties.

Many researchers already tried to fabricate $SmCo_5$ alloy nanomagnets by physical and chemical methods. As for a physical method, for example, monodispersed nanoparticles with an elemental composition of $SmCo_5$ were prepared by gas condensation with a cluster gun technique and treated by post annealing to transform to a $CaCu_5$ structure for magnetism.[9,10] However, the obtained particles hardly showed the coercivity at room temperature even after heat treatment. In contract, a chemical method has possibility to provide $SmCo_5$ nanomagnets. Since nanoparticles of both Sm and Co are easily oxidized by air, it is difficult to get particles with the correct elemental composition of $SmCo_5$ and the high coercivity at room temperature. There are two reports to attempt to prepare $SmCo_5$ nanomagnets. Oshima group reported that $SmCo_5$ nanoparticles prepared by a high-temperature solution-phase method showed a small coercivity at room temperature but did not have the composition of $SmCo_5$.[6] Gu and co-workers reported the preparation of $SmCo_5$ nanoparticles having the composition of $SmCo_5$ but not the coercivity at room temperature.[11] Quite recently, Teng and Yang reported the preparation of $SmCo_5$ nanoparticles coated by Fe_2O_3 shell, the coercivity of which was shown at 5 K but not at room temperature.[12]

In this paper, we propose the fabrication of $SmCo_x$ ($x =$ 5–8.5) nanoparticles by a polyol process by assistance of gold, i.e., reduction of $Sm(acac)_3 \cdot xH_2O$, $Co(acac)_3$, and AuCl in tetraethylene glycol. The prepared $SmCo_x$ nanoparticles had an average diameter of 6.9 nm, a crystal structure similar to $CaCu_5$, and the coercivity as high as 1500 Oe at room temperature.

While previous trials to fabricate $SmCo_5$ nanoparticles were carried out by using toxic $Co_2(CO)_8$ as a source of Co, we chose tris(acetylacetonate)cobalt(III) ($Co(acac)_3$) as a safe source of Co. The experiments for reduction of $Co(acac)_3$ and tris(acetylacetonate)samarium(III) ($Sm(acac)_3$) were carried out in tetraethylene glycol (TEG) at 270–280 °C for 1–5 h in the presence of oleic acid and oleylamine as protective agents.[13] The Sm–Co alloy nanoparticles obtained as powders gave a XRD pattern (Figure 1a), showing a cobalt-rich hcp (=hexagonal closed packing) crystal structure. Samarium(III) ions could not completely be reduced under the present conditions. Thus, we added a noble metal to the present reaction systems, because it was known that noble metal ions were easily reduced to from nanoparticles and that the noble metal nanoparticles often catalyze the reduction of other elements.[14] Thus, only 1 mol % of AuCl was added to the above-mentioned reaction system. The XRD pattern of powders obtained in this new system is shown in Figure 1b. Comparison of the XRD pattern of Figure 1b with that of $SmCo_5$ bulk in a literature shown in Figure 1c indicates that the prepared powders have a crystal structure similar to $CaCu_5$, originated from

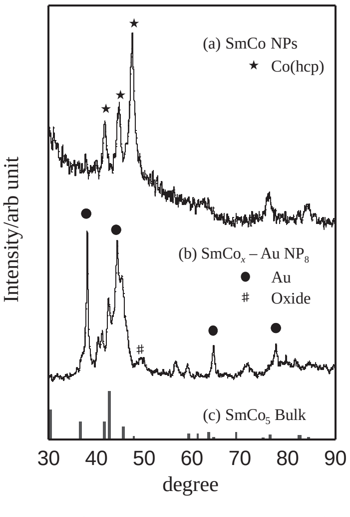

Figure 1. XRD pattern of (a) nanoparticles prepared from $Sm(acac)_3$ and $Co(acac)_3$ in TEG at 300 °C, (b) $SmCo_x$ ($x = 5$–8.5) nanoparticles chemically prepared by assistance of Au, and (c) $SmCo_5$ bulk.

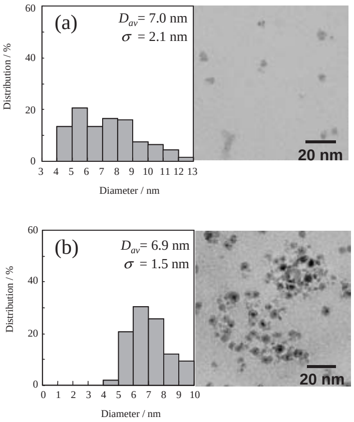

Figure 2. Transmission electron micrographs and particles size distribution histograms of (a) nanoparticles prepared from Sm(acac)$_3$ and Co(acac)$_3$ in TEG at 300 °C, and (b) SmCo$_x$ ($x = 5$–8.5) nanoparticles prepared from Sm(acac)$_3$ and Co(acac)$_3$ in TEG at 300 °C by assistance of Au.

SmCo$_5$ bulk. Moreover, the powders have also a face-centered cubic (fcc) crystal structure originated from gold bulk. Thus, it is suggested that the powders obtained in the presence of gold were composed of Au nanoparticles and SmCo$_5$ and/or Sm$_2$Co$_{17}$, i.e., SmCo$_x$ ($x = 5$–8.5) nanoparticles. However, the SmCo$_x$ nanoparticles look to be easily oxidized during the treatment, because the obtained SmCo$_x$ nanoparticles are contaminated with oxide judging by the observed XRD pattern.

Figure 2 shows transmission electron micrograph (TEM) of Sm–Co alloy powders prepared in the absence and presence of gold. In the absence of Au, the particle shape is a polygon and/or an aggregate having an average size of 7.0 nm. In the presence of Au, obtained particles have a relatively uniform size and a sharp size distribution with an average diameter of 6.9 nm. Results imply that the addition of Au has little influence on the shape and size of nanoparticles. The elemental analysis of nanoparticles, determined by ICP measurement, indicated that the powders prepared in the presence of Au were composed of Sm, Co, and Au at the ratio of 1:5.7:0.05.

Magnetic measurements of these particles were performed with a superconducting quantum interference device (SQUID) magnetometer. Blocking temperatures (T_B) of SmCo$_x$ nanoparticles estimated from curves of standard zero-field cooling and field cooling (ZFC and FC) vs. temperature plots were near room temperature, and the ferromagnetism was observed at above 300 K. The hysteresis loop of SmCo$_x$ nanoparticles at 300 K (Figure 3) exhibits a coerecivity (H_c) of 1500 Oe. However, the observed hysteresis loop is not so smooth, having some hollows. This is probably because of the influence of the third element Au added to the reaction system and in addition the oxidized products contaminated.

This will be the first report to produce SmCo$_x$ (SmCo$_5$ and/or Sm$_2$Co$_{17}$) nanoparticles having the coercivity at room temperature. We do not exactly know the reason for the production of SmCo$_x$ ($x = 5$–8.5) nanoparticles by addition of the third element Au to the reaction system. As we have aimed, Au nanoparticles, which can be easily produced by reduction of Au ions under the present reaction conditions, may play a role of the catalyst for reduction of Sm^{III} and/or Co^{III} ions by heat treatment in TEG at 300 °C. Another reason may possibly be easy formation of a CaCu$_5$ crystal structure from Sm and Co by assistance with Au^{I} ions and/or Au atoms.

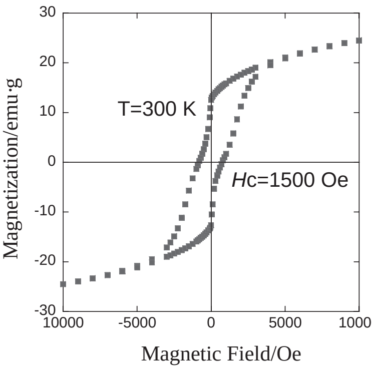

Figure 3. Applied magnetic-field dependence of the magnetization of the SmCo$_x$ ($x = 5$–8.5) nanoparticles at 300 K.

When Pt(acac)$_2$ was added to the reaction system of Sm(acac)$_3$ and Co(acac)$_3$ in TEG instead of AuCl, the similar effect of Pt was observed. Thus, preliminarily, SmCo$_x$ nanoparticles were obtained in this case, although they were contaminated with Co–Pt alloy nanoparticles instead of Au nanoparticles in the case of AuCl added. This result may support an idea of effect of the third element as the catalyst for reduction of Sm^{III} and/or Co^{III} ions. Addition of the third element to magnetic nanomaterials is often reported to decrease the phase-transfer temperature to a ferromagnetic crystal structure,[15] which is important to develop uniform nanomagnets for super-high-density magnetic memory. However, in the present case, the third element is used to promote direct formation of magnetic nonmaterials, which could be useful for development of others.

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