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Direct chemical synthesis of high coercivity air-stable SmCo nanoblades

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Ferromagnetic air-stable SmCo nanoparticles have been produced directly using a one-step chemical synthesis method. X-ray diffraction studies confirmed the formation of hexagonal SmCo₅ as a dominant phase. High resolution transmission electron microscopy confirms the presence of uniform, anisotropic bladelike nanoparticles approximately 10 nm in width and 100 nm in length. Values of the intrinsic coercivity and the magnetization in the as-synthesized particles are 6.1 kOe and 40 emu/g at room temperature and 8.5 kOe and 44 emu/g at 10 K, respectively. This direct synthesis process is environmentally friendly and is readily scalable to large volume synthesis to meet the needs for the myriad of advanced permanent magnet applications. © 2008 American Institute of Physics. [DOI: 10.1063/1.2963034]

Rare earth–transition metal (RE-TM) compounds with iron or cobalt as the TM constituent and one of the magnetic light REs, i.e., Pr, Nd, or Sm, as the RE constituent are especially well-suited for use as high-temperature, high-performance permanent magnets.^{1–12} In the RE-TM intermetallic compounds, the RE unpaired 4*f* electrons provide the magnetocrystalline anisotropy, which is potentially much stronger than the shape anisotropy, whereas the TM 3*d* electrons provide most of the magnetization and determine the Curie temperature. The Sm–Co binary equilibrium phase diagram indicates seven intermetallic compounds (RE:TM ratios 2:17, 1:5, 2:7, 1:3, 1:2, 9:4, and 3:1) that are stable under standard atmospheric conditions. Among these, SmCo₅ and Sm₂Co₁₇ are the most important permanent magnetic materials in the SmCo system. Both SmCo₅ and Sm₂Co₁₇ materials adopt hexagonal close packed (hcp) structures where Co dumbbell ion pairs are present in alternating layers along the crystallographic *c* axis. The easy magnetization direction of these SmCo intermetallic compounds is along the *c* axis and the room temperature magnetocrystalline anisotropy constant is of the order of 10⁸ erg/cm³.³ Furthermore, these compounds exhibit a very high Curie temperature (*T*_c=1020 K), which makes them superior to other classes of permanent magnetic materials, such as FePt (*T*_c=750 K) and Nd₂Fe₁₄B (*T*_c=585 K), for high-temperature applications. However, the high reactivity of SmCo nanoparticles renders them prone to rapid oxidation, making the synthesis of nanostructured SmCo₅ extremely difficult. Until now, two standard processing methods, i.e., ball milling and melt spinning, have been employed in the fabrication of nanostructured SmCo₅ magnets. However, these techniques provide limited control of the size and shape of the final magnetic particles. Solution-phase chemical synthesis approaches have been applied to the preparation of monodispersed magnetic nanoparticles¹³ and have been extended to the synthesis of SmCo₅ nanoparticles. Specifically, by coupling the reduction of samarium acetylacetonate, Sm(acac)₃, with the thermal decomposition of cobalt carbonyl, Co₂(CO)₈, SmCo particles

were formed.¹⁴ In Ref. 14, Sm and Co were demonstrated to possess the appropriate 1:5 molar ratio; however, there was no conclusive evidence that the hcp-structured SmCo₅ phase was formed nor were hard magnetic properties confirmed at room temperature. Recently SmCo₅ was synthesized by high-temperature reductive annealing of core/shell-structured Co/Sm₂O₃ nanoparticles¹⁵ at temperatures between 900 and 1100 °C under an inert atmosphere in the presence of metallic Ca and KCl. This calciothermic coreduction process is similar to the synthesis of bulk SmCo₅.³ The direct chemical synthesis of SmCo-based nanoparticles exhibiting high coercivity has been a long-standing goal for the magnetic materials community due to potential applications of these nanomagnets as high-performance permanent magnets and, most importantly, for their potential as aligned exchange-coupled nanocomposite magnets.^{16,17} Here we describe a direct chemical synthesis method to produce size-, shape-, and composition-controlled, highly coercive air-stable SmCo nanoparticles. This technique is based upon reduction of metal salts in a liquid polyol medium that acts as both a solvent and as a reducing agent for the synthesis of metal and alloy nanoparticles.¹⁸ The reduction reaction kinetics of the process are enhanced by (i) controlling the environment of the polyol medium and (ii) adding appropriate surfactants that limit the oxidation of RE ions when coreduced with TM particles. The RE-TM nanoparticles produced by this method may be further protected by application of an organic coating generated during the process from additives.

The synthesis of SmCo nanoparticles was carried out by employing mixtures of high-purity (99.99%) cobalt and samarium nitrates in the desired Co:Sm ratio dissolved in tetraethylene glycol. The total metal ion concentration was 0.02*M* in all experiments. The mixture was nitrogenated for approximately 1 h in a glove box. Poly(vinylpyrrolidone) was added as a capping agent to protect the particles from oxidation. The solution was heated between 373 and 573 K for various reaction times. After the mixture was cooled to room temperature, a black magnetic powder was recovered by centrifugation and rinsed in ethanol and redispersed in nonpolar solvents. It is noteworthy that the chemicals used in

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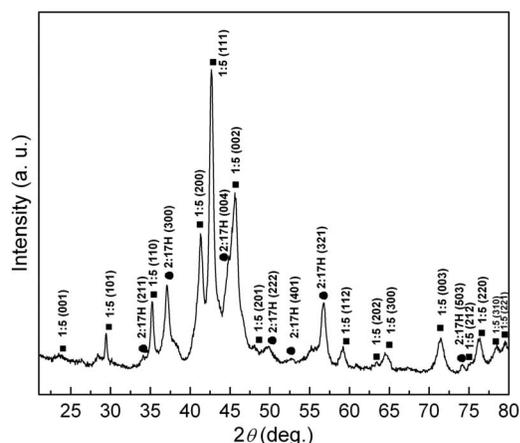


FIG. 1. XRD pattern of the as-synthesized air-stable SmCo nanoparticles prepared by direct chemical synthesis.

the processing of these particles are environmentally friendly and can be readily recycled during large scale synthesis.

The crystal structure of the as-synthesized SmCo nanoparticles was characterized by x-ray powder diffractometry (XRD) (Rigaku-Ultima III, Cu $K\alpha$ radiation). Elemental analyses were carried out using an energy dispersive x-ray analysis (Hitachi 2100). The size and morphology of the nanoparticles were characterized using a Tecnai F30 high-resolution transmission electron microscope (HRTEM) (300 kV) and low-resolution TEM JEOL 1010 (100 kV) instruments. Magnetic measurements for the randomly oriented particles mounted in a pyrex capsule were made with a Quantum Design physical property measurement system (PPMS 6000) under applied magnetic fields ranging between ± 6 T and at temperatures ranging from 10 to 300 K. Field cooled (FC) and zero field cooled (ZFC) thermomagnetic curves were measured from 10 to 350 K in an applied field of 100 Oe to investigate the magnetic uniformity of the sample. No demagnetization corrections were applied.

Since Sm has a very high negative reduction potential,¹⁹ i.e., -2.30 V, it is important to coreduce Sm and Co metal salt to successfully form SmCo nanoparticles. Researchers have found that the reduction rate of RE components is enhanced by introducing an appropriate amount of TM ions into liquid polyol.²⁰ For example, without Co ions the reduction of samarium alone is difficult even after 12 h of reaction time. However, when Co ions were introduced simultaneously with Sm ions in a polyol medium, a mixture of (fcc+hcp) Co phase with an intermediate amorphous Sm_2O_3 phase was formed. The formation of the intermediate Sm_2O_3 phase favors the rapid generation of dissolved Co species that are finally reduced to form crystalline SmCo nanoparticles. Figure 1 shows the XRD pattern of the SmCo nanoparticles prepared by the direct chemical synthesis method described here. The XRD data were collected under atmospheric conditions. No evidence of samarium oxide phases nor of metallic fcc/hcp Co or its oxides were observed even after exposed to air for six months. The diffraction peaks are indexed to standard patterns of the hexagonal phases of SmCo_5 (dominant phase) and $\text{Sm}_2\text{Co}_{17}$ (space group $P6/mmm$). The calculated lattice parameters for the SmCo_5 phase are $a=0.4991$ (± 0.002) nm and $c=0.3977$ (± 0.002) nm. These lattice parameters are to be compared with Ref. 21 bulk sample values of $a=0.4998$ nm and $c=0.3983$ nm. The experimental lattice parameters of the

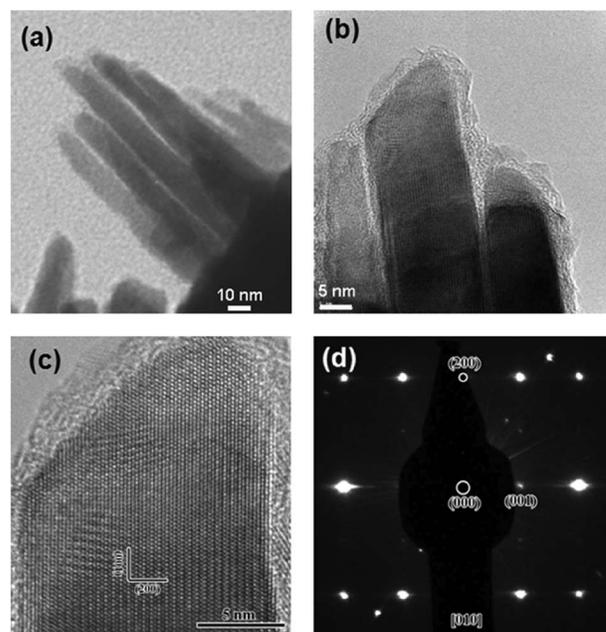


FIG. 2. (a) A low and (b) high magnification TEM image of the SmCo nanoblades. (c) HRTEM image showing the growth direction of the blade is $[100]$ (perpendicular to the (200) planes), and one of the surface plane parallel to the growth direction is the $\{001\}$ plane. (d) The electron diffraction pattern from the nanoblade shown in (c) indicating that the blade is orientated along the $[010]$ zone axis, and is consistent with the HRTEM image, showing the SmCo_5 phase.

$\text{Sm}_2\text{Co}_{17}$ phase are $a=0.8367$ (± 0.002) nm and $c=0.8192$ (± 0.002) nm, and should be compared with the (Ref. 22) values of $a=0.8373$ nm and $c=0.8165$ nm. The air-stable SmCo samples also contain trace amounts of the rhombohedral 2-17 phase as indicated by the presence of the (202) peak appearing at $2\theta=28.67^\circ$. The diffraction peak intensity ratios for the as-synthesized SmCo_5 particles (i.e., $I_{111} > I_{200} > I_{110} > I_{101}$) are different from those for the bulk SmCo_5 (i.e., $I_{111} > I_{101} > I_{110} \sim I_{200}$). We attribute this anomaly to the anisotropic morphology of the SmCo particles. Further, the anisotropic morphology of the SmCo particles was substantiated by the TEM analysis while selected area electron diffraction (SAED) showed similar crystallographic sample texturing.

Elemental mapping analysis of the nanoparticles carried out using field emission scanning electron microscopy (Carl Zeiss SUPRA25) indicated that Sm and Co are evenly distributed in the particles. Figures 2(a)–2(c) show low and high magnification TEM images of the SmCo nanoblades synthesized at the reaction temperature of 573 K, respectively. It is evident that the as-synthesized air stable hcp-SmCo nanoparticles exhibit high crystallinity with an anisotropic bladelike structure. One can clearly see from Fig. 2(a) that there is no evidence supporting the presence of small/second degree particles in these samples. Later, we discuss FC and ZFC thermomagnetic results that further substantiate these data. The nanoblades have a uniform morphology with an average width of ~ 10 nm and length of ~ 100 nm. Subsequent experiments, not reported here, indicate that the size and morphology of the particles (nanoblades, nanospheroids, and nanospheres) is strongly dependent on the reaction conditions.²³ The high-resolution TEM image, Fig. 2(c), indicates that each blade is a single crystal with hexagonal stacking of layers, and the growth direction of the blade is along the $\langle 100 \rangle$ direction (perpendicular to the (200) planes),

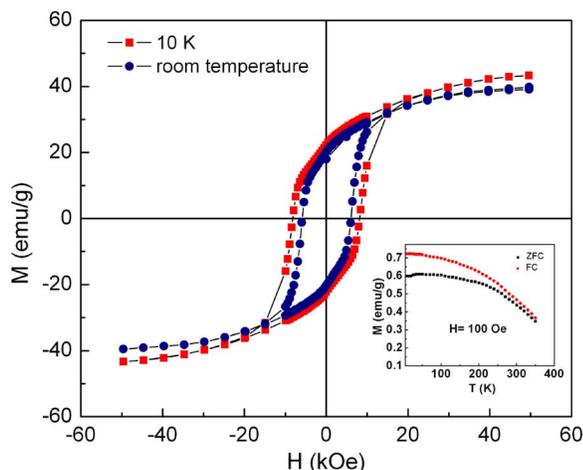


FIG. 3. (Color online) Hysteresis loops of air-stable SmCo nanoblades measured at room temperature and 10 K. Inset: temperature dependence of FC and ZFC dc magnetization measured under an applied magnetic field of 100 Oe.

and demonstrates that one of the surface planes parallel to the growth direction, i.e. $\{001\}$. The SAED pattern obtained from the nanoblade, Fig. 2(d), indicates that the blade is a single crystal, orientated along the $[010]$ zone axis, consistent with the HRTEM image showing the SmCo₅ phase. The SAED shows weak streaks along the $[001]$ direction, indicating stacking faults exist along the c -axis direction. The anisotropic air-stable SmCo nanoblades have significant potential for easy-axis (i.e., c axis) orientation of the particles under the application of low magnetic fields to produce oriented permanent magnetic compacts. Furthermore, the elongated nanoparticles possess a shape anisotropy that will augment the magnetocrystalline anisotropy to foster high energy products.

The as-synthesized air-stable SmCo nanoblades exhibit ferromagnetism at room temperature. It can be seen from Fig. 3 that the values of the intrinsic coercivity and the magnetization of the nanoparticles are 6.1 kOe and 40 emu/g at room temperature, and 8.5 kOe and 44 emu/g at 10 K, respectively. The shape of the initial magnetization curve suggests that the coercivity develops via a pinning mechanism²⁴ (not shown here). The high coercivity observed for the as-synthesized nanoblades is likely due to a combination of shape and magnetocrystalline anisotropy. The inset to Fig. 3 shows the temperature dependence of FC and ZFC magnetization curves acquired for as-synthesized SmCo nanoblades with an applied magnetic field of 100 Oe. These data indicate a blocking temperature (T_B) greater than 350 K. The large difference between the FC and ZFC trends suggest that the SmCo nanoparticles are larger than the superparamagnetic limit which would be evident in the thermomagnetic data.

In summary, we have developed a direct chemical synthesis method to produce air-stable high coercivity SmCo nanoparticles. Additional heat treatment procedures are not required to realize high intrinsic coercivity and high magnetization. XRD studies confirm the formation of hcp-SmCo nanoparticles while HRTEM micrographs reveal a bladelike morphology in which the dimensions are ~ 10 nm in width and ~ 100 nm in length. Values of the intrinsic coercivity and

the magnetization for the as-synthesized particles are 6.1 kOe and 40 emu/g and 8.5 kOe and 44 emu/g, at room temperature and 10 K, respectively. Our findings suggest that these nanoblade particles are appropriate for the synthesis of high energy-product single-phase and nanocomposite RE-TM magnetic compacts that may satisfy the needs for advanced permanent magnets, magnetic and magneto-optical recording media, and biomedical applications. The process described here may be readily scaled for large volume industrial synthesis at modest costs and is anticipated to prove effective as an alternative means of producing high energy product RE-TM magnets. Further, the chemistry used in the processing is environmentally friendly and can be readily recycled during large scale synthesis. This work makes clear that direct chemical synthesis of RE-TM nanoparticles with well-controlled shapes, sizes, and structures is a practical reality.²⁵

This work was performed, in part (i.e., HRTEM), at the Center for Integrated Nanotechnologies, a U.S. Department of Energy, Office of Basic Energy Sciences user facility. Sandia National Laboratories is a multiprogram laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the U. S. Department of Energy under Contract No. DE-AC04-94AL85000.

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