OPEN

Enhancement of anisotropy energy of SmCo_5 by ceasing the coupling at 2c sites in the crystal lattice with Cu substitution

Syed Kamran Haider^{1,2,3}, Hieu Minh Ngo¹, Dongsoo Kim^{2,3} & Young Soo Kang¹✉

SmCo_5 and $\text{SmCo}_{5-x}\text{Cu}_x$ magnetic particles were produced by co-precipitation followed by reduction diffusion. HRTEM confirmed the Cu substitution in the SmCo_5 lattice. Non-magnetic Cu was substituted at "2c" site in the SmCo_5 crystal lattice and effectively stopped the coupling in its surroundings. This decoupling effect decreased magnetic moment from SmCo_5 ($12.86 \mu_B$) to SmCo_4Cu ($10.58 \mu_B$) and SmCo_3Cu_2 ($7.79 \mu_B$) and enhanced anisotropy energy from SmCo_5 (10.87 Mega erg/cm³) to SmCo_4Cu (14.05 Mega erg/cm³) and SmCo_3Cu_2 (14.78 Mega erg/cm³). Enhancement of the anisotropy energy increased the coercivity as its values for SmCo_5 , SmCo_4Cu and SmCo_3Cu_2 were recorded as 4.5, 5.97 and 6.99 kOe respectively. Being six times cheaper as compared to Co, substituted Cu reduced the price of SmCo_3Cu_2 up to 2%. Extra 15% Co was added which not only enhanced the M_r value but also reduced the 5% of the total cost because of additional weight added to the SmCo_3Cu_2 . Method reported in this work is most energy efficient method on the synthesis of Sm–Co–Cu ternary alloys until now.

Among permanent magnet materials, SmCo_5 constitute the second strongest class of magnets. With the K_u value larger than 1.19×10^8 erg/cm³ SmCo_5 alloy has a very high uni-axial magneto-crystalline anisotropy and the highest Curie temperature among permanent magnetic materials^{1–7}. Because of high curie temperature they also have special applications, such as high-end engines in motorsports, where magnets are exposed to temperatures above 240 °C. Transition metals substitution for Co into SmCo_5 can change the values of coercivity, M_r and M_s ^{8–11}. It was theoretically predicted that by substitution of Cu with Co, coercivity of SmCo_5 can be increased on the expense of M_r and M_s values¹². Decrease in the M_r is the serious disadvantage that reduces the energy density/ BH_{max} despite of enhancement of the coercivity.

Second disadvantage associated with SmCo_5 magnets is their high cost. Sm is the most expensive element among its group and Co is also more expensive than Fe and these make the SmCo_5 most expensive class of the permanent magnets. Biggest reason behind high cost of SmCo_5 is the low quantity of the Sm and Co in the earth crust as shown in Fig. S-1-a. Cu is almost twice abundant (0.0068%) as compared to the Co (0.0003%) in the earth crust and this is one of the reasons that it is six times cheaper as compared to the Co (Fig. S-1-b). Another reason for the low price of Cu is the acquisition of Cu as the byproduct, during the extraction of Co from ores by pyro-metallurgy, hydro-metallurgy, and vapor-metallurgical methods¹³. Hence some ores those are primarily source of the Co (e.g. Carrolite) are also an important source of Cu.

Cu substitution for the Co can reduce the cost of most expensive magnet, SmCo_5 . But the price of SmCo_5 is critically determined by the Sm due to the high price of Sm (750 USD/kg) as compared to the Co (28 USD/kg). Although Co is six times more expensive as compared to the Cu but Co substitution with Cu (in SmCo_3Cu_2) decreases the price of the magnet produced, only up to 2%. Another important factor that may reduce the price of the SmCo_3Cu_2 is use of extra fused Co phase. This extra Co not only enhances the magnetic properties but also increases the overall weight of the produced SmCo_3Cu_2 . SmCo_5 consists of almost 33% of Sm by weight, hence 15% addition of Co saved the 5% of the Sm. By considering both the factors (substitution of Co with Cu and addition of extra Co), overall price of SmCo_3Cu_2 could be reduced up to 6%. Reduced price of the SmCo_5

¹Department of Chemistry, Sogang University, 35, Baekbeomro, Mapogu, Seoul 04107, South Korea. ²Powder and Ceramics Division, Korea Institute of Materials Science, Changwon, Gyeongnam 51508, South Korea. ³Convergence Research Center for Development of Mineral Resources, Korea Institute of Geoscience and Mineral Resources, Daejeon 34132, South Korea. ✉email: yskang@sogang.ac.kr

in this work may have a large impact, because global market value of the SmCo_5 magnet produced per year is approaching worth 1 billion USD in near future (Fig. S-1-c).

Third problem with the synthesis of Sm–Co–Cu ternary alloys is the high consumption of energy. Te'llez-Blanco et al.^{14,15} annealed Sm, Co and Cu for 504 h (21 days) at 1000 °C. Nishida et al. performed the annealing at more than 800 °C for 160 h¹⁶. Gabay et al. annealed the Sm, Co and Cu for 100 h (50 h at 1050 °C then 50 h 350–450 °C)¹⁷. Researchers those did not use simple annealing, used expensive methods like sputtering, arc melting, electron beam heating and Induction melting. Even after induction melting at 1430 °C, Suresh et al. later annealed the sample at 900 °C for 4 h for homogenization¹⁸. Annealing at such high temperature also leads to the loss of Sm which is evaporated and compensated with the addition of extra Sm. In this work reduction diffusion method is used for the synthesis of the magnetic particles which energy and time efficient as compared to the regular physical methods^{19–22}.

This study suggests an eco-friendly chemical method for the synthesis of the Cu substituted SmCo_5 particles. In this energy efficient process, precursors were annealed at 900 °C for only 2 h. Cu substitution enhanced the coercivity, while reduction in the Mr value caused by Cu substitution is compensated by addition of extra Co. Cost of the SmCo_5 is reduced by substitution of Cu with Co. Extra added Co also increased the weight of $\text{SmCo}_{5-x}\text{Cu}_x$ magnet which further reduced its cost.

Experimental section

Materials. Samarium chloride ($\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$, 99% purity), cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), copper chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 99% purity), and potassium chloride (KCl, 99% purity) were obtained from Sigma Aldrich. 16 mesh granular Ca (99.5% purity) was obtained from Alfa Aesar. These reagents were used without further purification. Milli-Q IQ 7000 water purifying system was used to obtain deionized water.

Preparation of SmCo_5 and $\text{SmCo}_{5-x}\text{Cu}_x$ particles. In the first step, chloride precursors were changed to hydroxides by the co-precipitation method. Chloride compounds of Sm, and Co and Cu were dissolved in DI water. $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ were used as precursors and their molar masses were noted as 364.8, 237.95 and 170.48 g/mol respectively. In order to prepare SmCo_5 , Sm:Co molar ratio was kept as 1:4.2. Hence, 2.379 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and 0.870 g of $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 100 ml of de-ionized water. Extra Sm precursor was used because some Sm is evaporated during the reduction-diffusion process.

For synthesis of SmCo_4Cu and SmCo_3Cu_2 , Sm:Co:Cu molar ratios were kept as 1:3.36:0.84 and 1:2.52:1.68 respectively. 15% extra Co was further added to the $\text{SmCo}_{5-x}\text{Cu}_x$ that changed the Sm:Co:Cu molar ratio. Hence, for SmCo_4Cu Molar ratio of Sm:Co:Cu was taken as 1:3.86:0.86. Meanwhile for SmCo_3Cu_2 Molar ratio of Sm:Co:Cu was taken as 1:2.90:1.68.

Experimentally for synthesis of SmCo_4Cu , $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ (0.870 g), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (2.186 g) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.341 g) were dissolved in 100 ml of water. Meanwhile for synthesis of SmCo_3Cu_2 , $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ (0.870 g), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (1.643 g) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.682 g) was dissolved in 100 ml of water.

A 3.5 M NaOH solution was added drop-by-drop to raise the pH of the solution up to 13, so that all of the metal chlorides could be changed to metal hydroxide. The reaction mixture was stirred continuously during the addition of NaOH solution. While maintaining the pH at 13, the solution was stirred for 1 h. Then, products were washed twice with DI water and ethanol, and dried at 80 °C for 1 h. XRD, TEM, and TEM-EDS analysis of SmCoCu hydroxides are provided as Fig S-2, S-3 and S-4 and S-5 in supporting information. The second step was the reduction-diffusion reaction. Hydroxides obtained from the first step were mixed with Ca and KCl in a glove box and then pressed into pellet form. Weight ratio of Ca, hydroxides and KCl was kept as 6:1:1. The pellet was reduced and diffused in a tube furnace by heating at 900 °C for 2 h, while Ar was flowing in the furnace. CaO produced during R-D can reduce the magnetic properties^{23,24}. Hence, the product was washed with water again and again to remove CaO completely and washed twice with acetone before being stored in inert conditions. All steps of the experimental procedures are shown in Fig. S-6. Mechanism of the reactions occurred during the experiment is explained in the supplementary information.

Characterization. Crystal structure analysis was done with X-ray diffractometer (Rigaku MiniFlex) with Cu-K α source radiation wavelength of 0.15418 nm. EDX, TEM and HRTEM characterizations were done on JEM-2100F by JEOL Ltd. For these characterizations SmCo_5 and $\text{SmCo}_{5-x}\text{Cu}_x$ samples were dispersed in hexane and the intermediate co-precipitation product samples were dispersed in ethanol. Ni TEM grid was used for TEM and HRTEM analyses. Magnetic properties (demagnetization curves) of SmCo_5 and $\text{SmCo}_{5-x}\text{Cu}_x$ products were measured by Physical Property Measurement System (PPMS, Evercool II–9T) in the vibrating sample magnetometer mode.

Results and discussion

SmCo_5 and $\text{SmCo}_{5-x}\text{Cu}_x$ particles were produced by the experimental process described in the experimental section. XRD patterns for all SmCo_5 and $\text{SmCo}_{5-x}\text{Cu}_x$ particles produced are similar (Fig. 1a) because the crystal structure of these products is quite similar. Co and Cu have nearly similar atomic radii (125 pm and 128 pm respectively) but these variations are detectable. Hence, there is slight enhancement in the d-spacing in the crystal of $\text{SmCo}_{5-x}\text{Cu}_x$ because of substitution of Co with Cu. This enhanced d spacing also shifts the peak to the smaller value of theta (θ) in XRD pattern (Fig. 1b). Cobalt peak is also observed around 45° (Fig. 1a) in $\text{SmCo}_{5-x}\text{Cu}_x$.

SEM images in Fig. 1 reveal that the particles of all three products are in irregular shape and the size varies from 0.1 to 10 μm . Apparently it seems that Cu substitution enhances the particle size but exact mechanism behind this increased size is yet unknown. Maybe this due to faster reduction-diffusion in $\text{SmCo}_{5-x}\text{Cu}_x$ as compared to the SmCo_5 . Hence $\text{SmCo}_{5-x}\text{Cu}_x$ particles are formed earlier (as compared to the SmCo_5) and stay for

Figure 1. (a) XRD patterns of SmCo₅, SmCo₄Cu, and SmCo₃Cu₂. (b) Slight peak shift in XRD patterns of SmCo₅, SmCo₄Cu and SmCo₃Cu₂. SEM images of (c) SmCo₅ (d) SmCo₄Cu and (e) SmCo₃Cu₂. Particle size distribution of (f) SmCo₅ (g) SmCo₄Cu and (h) SmCo₃Cu₂.

longer time at 900 °C. More annealing time can lead to the Ostwald ripening and resulted in increased size of particles.

Sm, Co and Cu are distributed evenly in the SmCo_{5-x}Cu_x particles as shown in EDX mapping image of Fig. 2 that indicates the complete formation of SmCo_{5-x}Cu_x alloy particles. TEM-EDS of SmCo₅ is provided in supplementary information as Fig. S-7. Figure 2e is EDS line analysis of an isolated SmCo₄Cu line. Line mapping confirms the homogeneous distribution of Cu throughout the particle. This also suggests the presence of Cu in the SmCo₄Cu crystal, as elemental distribution is very regular. However, density of Sm, Co, and Cu is much higher in the center of the particle. This is because of higher thickness of the particle in the center. Small cobalt particles are attached on SmCo₃Cu₂, can be detected in TEM-EDS images, Fig. 2f–i. Schematic illustration of SmCo₃Cu₂/Co interface is explained in Fig. 2j²⁵.

There is possibility that Co particles detected in TEM-EDS might be left after the reduction diffusion process and now exist as the free detached, Co particles in SmCo₄Cu, and SmCo₃Cu₂. Other possibility is that these Co particles were fused with SmCo₄Cu, and SmCo₃Cu₂ at high temperature during the reduction diffusion process, which was further proved by HRTEM analysis. Fused Co is identified at [100] facet in Fig. 3a. A portion of Fig. 3a, shown in red dotted box is zoomed in and described as Fig. 3b. Rhombus shown in Fig. 3d connects the four Sm atoms in the [001] zone axis. There are three Co atoms between these four Sm atoms but not visible in the TEM image because of their small size. Figure 3c is the modeling of SmCo₅ structure which is taken along “a/b” axis showing four Sm atoms connected by rhombus²⁵.

Figure 3d is the hexagonal cubic pack structure of the SmCo_{5-x}Cu_x/SmCo₅. These four Sm atoms are arranged in the “a/b” axis of the crystal lattice. HRTEM analysis confirms the presence of Co and SmCo₃Cu₂ phases and their fusion in a single particle.

Figure 2. (a–d) TEM-EDS mapping images and (e) EDS line analysis of SmCo_4Cu . (f–i) TEM-EDS mapping images SmCo_3Cu_2 and (j) schematic illustration of Co attachment on SmCo_3Cu_2 .

During annealing at 900 °C, reduced oxides of Sm, Co and Cu were ready to diffuse and form new crystal. At 727 °C, Cu has lower enthalpy of the reduction (172.8 kJ/Mol) as compared to the Co (238.4 kJ/Mol)²⁶. Hence Cu reduces and diffuses much faster than Co and all Cu becomes the part of the $\text{SmCo}_{5-x}\text{Cu}_x$ crystal lattice (Fig. 3e). Left over Co is found as fused Co phase, detected in XRD, HRTEM and EDS mapping. Sm and Co are distributed in the two layers of hcp crystal SmCo_5 , with the similar atomic distribution found in CaCu_5 type crystals²⁷. These layers are “3g” and “2c”. Co always occupies 3g layer. “2c” layer is shared among Co and Sm, where Sm are on the edges of the SmCo_5 crystal and Co is located between the Sm atoms. Cu substitutes the Co in “2c” layer (Fig. 3e) and enhances the magneto-crystalline anisotropy¹². Instability of Cu substitution at 3g sites is also confirmed by previous studies^{12–28}. Cu substitution has been clearly explained (Fig. 4) with top and side view of arrangement of the atoms in SmCo_5 and $\text{SmCo}_{5-x}\text{Cu}_x$.

Enhancement in the crystal parameters “a, b, c” and crystal volume was recorded after substitution. SmCo_5 and $\text{SmCo}_{5-x}\text{Cu}_x$ have hexagonal close pack crystal structure. Crystal parameters in the hcp were calculated with the help of the following equation as reported by the Sinha et al.²⁹

$$\frac{1}{(d_{hkl})^2_{\text{hcp}}} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a_{\text{hcp}}^2} \right) + \frac{1}{c_{\text{hcp}}^2}$$

“d” and “hkl” values were determined from the XRD patterns. Peak with [200] facet was selected and “d” spacing value for the [200] facet was determined from the XRD patterns. By putting the value of “d” in the equation above, value of the “a” parameter was calculated.

Figure 3. (a) HRTEM of SmCo_3Cu_2 , (b) zoomed in area from the red dotted box in Fig. 2-a, (c) modeled SmCo_5 structure, taken along “a/b” axis, (d) $\text{SmCo}_{5-x}\text{Cu}_x/\text{SmCo}_5$ hcp crystal structure and (e) arrangements of atoms in the SmCo_5 crystal lattice and the mechanism of Co substitution with Cu in “2c” layer of $\text{SmCo}_{5-x}\text{Cu}_x$ crystal lattice.

In the next step peak with the [111] facet was selected. Then “d” value for the [111] facet was determined and were put in the equation above. With the already known value of “a” parameter, value of “c” parameter was determined. In the hcp crystal “a = b”, hence no calculations for the “b” were performed. Substitution increased the unit cell volume by 3.9% (SmCo_4Cu) and 5% (SmCo_3Cu_2) as shown in the Fig. 4. Collectively, all the crystal parameters were increased after the substitution.

With electronic configuration of $[\text{Xe}] 4f^6 6s^2$, Sm has 6 unpaired electrons in 4f orbital. Before coupling with Co, electrons in the “f” orbital of Sm hybridize and move to the 5d orbital. Hence actual electronic configuration of the Sm in SmCo_5 is $[\text{Xe}] 5d^6 6s^2$ and it has four unpaired electrons in the valance shell. However, after the hybridization, 5d electrons are in the spin down state³⁰. Valance unpaired electrons in Co are in spin up configuration, hence Sm couples antiferro-magnetically with the Co (Fig. 5a). Co with electronic configuration of $[\text{Ar}] 3d^7 4s^2$ has three unpaired electrons in 3d orbital. Co has all the unpaired 3d electrons in the spin up configuration, which confirms that Co–Co exchange coupling is ferromagnetic (Fig. 5a).

Cu has electronic configuration of $3d^{10} 4s^1$ therefore it does not have any unpaired electron in the valance shell. Hence Cu being non-magnetic, does not couple with Co or Sm either (Fig. 5b).

When one Co, Cu or Sm atom come contact with the other Co, Cu or Sm atoms, their valance electrons make a valance band. This valance band can be explained with rigid band model (Fig. 5c). Density or abundance of the electrons is taken on X-axis while energy of electrons is taken on the Y-axis. E_f (fermi level) of the rigid band of the Cu is located in the “s” orbital which indicates that “3d” orbital is completely filled. It further tells that there is no inter-orbital movement of electrons in between 3d and 4s orbitals. All electrons in 3d orbitals are retained there unpaired therefore, being non-magnetic there is no chance for the Cu to couple with Sm or Co either. In case of Sm or Co, energy level of 3d electrons is similar to the 4s electrons, hence movement of electrons between the 4s and 3d orbital is possible. Fermi level of the Sm and Co is almost in the center of 3d band therefore, 3d band is partially filled (Fig. 4). Conclusively these band in Sm and Co are magnetic and can couple with each other.

Cu reduced magnetic moment more effectively when it substitutes Co at “2c” position. Substitution at “3g” site can eliminate the anisotropy energy, in consequence magnetic properties may vanish¹². SmCo_4Cu or SmCo_3Cu_2 are anisotropic and easily magnetized from the a/b dimension of the crystal lattice (Fig. 6a). “2c” site substitution can decouple the ferromagnetic interaction between cobalt atoms of “2c” and “3g” layers and magnetic moment between these layers reduces drastically. Hence magnetization in the a/b direction (easy direction for magnetization) of the crystal becomes harder, that leads to the enhancement of coercivity and reduction of Mr value. It is concluded that in this work substitution occurred at the “2c” site as shown in the Fig. 6a.

Being non-magnetic after substitution, Cu strongly affects the magnetic properties of SmCo_5 . Measured magnetic hysteresis curves for the $\text{SmCo}_{5-x}\text{Cu}_x$ and $\text{SmCo}_{5-x}\text{Cu}_x$ are shown in Fig. 6b. The magnetic moment of SmCo_5 , SmCo_4Cu and SmCo_3Cu_2 are to be 12.86, 10.58 and 7.79 μ_B , respectively. In our work magnetic moment for SmCo_5 and $\text{SmCo}_{5-x}\text{Cu}_x$ was calculated from the M_s values in the hysteresis loop. These values are lower than theoretically calculated values, because the theoretical conditions are ideal conditions (e.g. no thermal energy in the system and no oxidation of the product). The measured hysteresis curves for the SmCo_5 and $\text{SmCo}_{5-x}\text{Cu}_x$ are shown in Fig. 6b.

Reduction in magnetic moment critically affected on the anisotropy energy and coercivity. Coercivity (H_c) values of SmCo_5 , SmCo_4Cu and SmCo_3Cu_2 were recorded as 4.5, 5.97 and 6.99 kOe, respectively. The increasing

Figure 4. (a) Top and side view of arrangement of the atoms in SmCo_5 and $\text{SmCo}_{5-x}\text{Cu}_x$, (b) space-filling model of SmCo_5 and $\text{SmCo}_{5-x}\text{Cu}_x$ with crystal dimensions, (c) crystal parameters of SmCo_5 and $\text{SmCo}_{5-x}\text{Cu}_x$.

order of coercivity of all three products was determined as $\text{SmCo}_5 < \text{SmCo}_4\text{Cu} < \text{SmCo}_3\text{Cu}_2$. Simultaneously decreasing order of magnetic moment is $\text{SmCo}_5 > \text{SmCo}_4\text{Cu} > \text{SmCo}_3\text{Cu}_2$.

Energy density or energy product is intrinsic property and is the amount of energy stored in the lattice because of arrangement of the atoms in the crystal. It was found that Cu substitution enhanced the energy density. Energy densities for SmCo_5 , SmCo_4Cu and SmCo_3Cu_2 were recorded as 10.87, 14.05, and 14.78 M erg/cm³ respectively. Furthermore, it is also evident from the hysteresis loop that squareness ratio was also increased after the Cu substitution. Complete hysteresis loop is given in the supplementary information as Fig. S-8. Possible effect of Cu substitution on the domain wall of $\text{SmCo}_{5-x}\text{Cu}_x$ is also explained in the supplementary information.

Role of the extra Co phase present in the $\text{SmCo}_{5-x}\text{Cu}_x$ is very important. Cu enhances the coercivity at the cost of magnetic moment. Formation of SmCo_3Cu_2 after the substitution of Cu in SmCo_5 can reduce the M_r value up to 35%¹² and 32%³¹. Reduced M_r value will reduce the energy density drastically despite of enhancement of the coercivity. Purpose of keeping the extra Co phase was to maintain the M_r value as well as the cost reduction of the product. Proposed mechanism of reduction of M_r value by coupling between Co and SmCo_3Cu_2 is explained in Fig. S-9.

Coercivity of the SmCo_5 particles produced by chemical method is quite low as compared to the SmCo_5 magnets. But the coercivity reported in our work is still relatively lower as compared to the coercivity reported in other recent chemical methods. One reason behind the lower value of the coercivity is the presence of small $\text{Sm}_2\text{Co}_{17}$ phase (Fig. 1). Second main reason for the lower coercivity value is the irregular size and morphology of the magnetic particles. It is common observation, that when particle size of magnetic powder approaches the single domain size, magnetic properties are excellent. Similar conclusion was concluded by the Ma et al.⁵ and they provided the magnetic properties of the mono-dispersed particles. Chuev et al. and Chen et al. explained the size and morphology dependence of magnetic properties (especially coercivity in detail)^{32,33}. In our work, particles with the similar size (average size 300 nm) were also separated and they exhibited much better magnetic

Figure 5. (a,b) Schematic illustration of exchange coupling between the electrons of Sm, Co and Cu, (c) rigid band model of Sm, Co and Cu.

properties. Coercivity of SmCo_3Cu_2 was recorded as 13.5 kOe. Detail of this experiment and results obtained is described in the supplementary information.

Conclusion

SmCo_5 and $\text{SmCo}_{5-x}\text{Cu}_x$ magnetic particles were synthesized by energy efficient, chemical method. Microstructure confirmed the Cu substitution in the SmCo_5 lattice and presence of Co phase fused together with $\text{SmCo}_{5-x}\text{Cu}_x$. After substitution at “2c” site in the SmCo_5 crystal lattice, Cu almost blocked the coupling in the surrounding. The resulted decoupling in the crystal lattice affected the magnetic moment, anisotropy and coercivity. Magnetic moment was reduced as the result of Cu substitution, but coercivity and anisotropy energy were enhanced. The substitution of Co with Cu and extra Co phase decreased the price of $\text{SmCo}_{5-x}\text{Cu}_x$, up to 5%.

Figure 6. (a) Mechanism on the reduction of exchange coupling before and after Cu substitution in SmCo₅ and SmCo_{5-x}Cu_x. (b) Magnetic hysteresis loops of SmCo₅ and SmCo_{5-x}Cu_x. Variation of magnetic moment, H_c , M_r , M_s and anisotropy energy, before and after Cu substitution.

Received: 17 January 2021; Accepted: 22 April 2021

Published online: 12 May 2021

References

- Weller, D. *et al.* High K_u materials approach to 100 Gbits/in²M. *IEEE Trans. Magn.* **36**, 10–15 (2000).
- Liu, F., Hou, Y. L. & Gao, S. Exchange-coupled nanocomposites: Chemical synthesis, characterization and applications. *Chem. Soc. Rev.* **43**, 8098–8113. <https://doi.org/10.1039/C4CS00162A> (2014).
- Li, H. L., Guo, D. F., Lou, L., Li, W. & Zhang, X. Y. Three-dimensional self-assembly of core/shell-like nanostructures for high-performance nanocomposite permanent magnets. *Nano Lett.* **16**, 5631–5638. <https://doi.org/10.1021/acs.nanolett.6b02210> (2016).
- Zhang, T., Liu, H. Y., Liu, J. H. & Jiang, C. B. 2:17-type SmCo quasi-single-crystal high temperature magnets. *Appl. Phys. Lett.* **106**, 162403. <https://doi.org/10.1063/1.4918939> (2015).

5. Ma, Z. H., Zhang, T. L. & Jiang, C. B. A facile synthesis of high performance SmCo_5 nanoparticles. *Chem. Eng. J.* **264**, 610–616. <https://doi.org/10.1016/j.cej.2014.11.138> (2015).
6. Shen, B. *et al.* Chemical synthesis of magnetically hard and strong rare earth metal based nanomagnets. *Angew. Chem.* **131**, 612–616. <https://doi.org/10.1002/anie.201812007> (2019).
7. Li, Y., Zhang, X. L., Qiu, R. & Kang, Y. S. Synthesis and investigation of SmCo_5 magnetic nanoparticles. *Colloid. Surf. A Physicochem. Eng. Aspects* **313**, 621–624. <https://doi.org/10.1016/j.colsurfa.2007.04.150> (2008).
8. Zhou, J., Skomski, J. R., Chen, C., Hadjipanayis, C. J. & Sellmyer, D. J. Sm–Co–Cu–Ti high-temperature permanent magnets. *J. Appl. Phys. Lett.* **77**, 1514–1516. <https://doi.org/10.1063/1.1290719> (2000).
9. Goll, D., Kleinschroth, I., Sigle, W. & Kronmüller, H. Melt-spun precipitation-hardened $\text{Sm}_2(\text{Co}, \text{Cu}, \text{Fe}, \text{Zr})_{17}$ magnets with abnormal temperature dependence of coercivity. *Appl. Phys. Lett.* **76**, 1054–1056. <https://doi.org/10.1063/1.125936> (2000).
10. Hadjipanayis, G. C. *et al.* High temperature 2:17 magnets: Relationship of magnetic properties to microstructure and processing. *IEEE Trans. Magn.* **36**, 3382–3433. <https://doi.org/10.1109/20.908808> (2000).
11. Liu, S., Yang, J., Doyle, G., Potts, G. & Kuhl, G. E. Abnormal temperature dependence of intrinsic coercivity in sintered Sm–Co-based permanent magnets. *J. Appl. Phys.* **87**, 6728. <https://doi.org/10.1063/1.372822> (2000).
12. Cheng, W., Yifan, D., Hao, H., Xiaomin, C. & Miao, X. Effect of Cu substitution on the magnetic properties of SmCo_5 film with perpendicular magnetic anisotropy. *J. Electron. Mater.* **41**(8), 2178–2183. <https://doi.org/10.1007/s11664-012-2119-1> (2012).
13. Michael, T. O., Tej, N. L., Sergey, L. B., Paul, C. C. & Andriy, P. Structural and magnetic properties of the CeCo_5 – CeZn_5 solid solution and potential improvements upon iron substitution. *J. Magn. Magn. Mater.* **482**, 192–200. <https://doi.org/10.1016/j.jmmm.2019.03.024> (2019).
14. Téllez-Blanco, J. C., Grössinger, R. & Turtell, R. S. Structure and magnetic properties of $\text{SmCo}_{5-x}\text{Cu}_x$ alloys. *J. Alloys Compd.* **281**, 1–5. [https://doi.org/10.1016/S0925-8388\(98\)00760-9](https://doi.org/10.1016/S0925-8388(98)00760-9) (1998).
15. Téllez-Blanco, J. C., Turtelli, R. S., Grössinger, R., Estévez-Rams, E. & Fidler, J. Giant magnetic viscosity in $\text{SmCo}_{5-x}\text{Cu}_x$ alloys. *J. Appl. Phys.* **86**, 5157–5163. <https://doi.org/10.1063/1.371493> (1999).
16. Nishida, I. & Uehara, M. Study of the crystal structure and stability of pseudo-binary compound $\text{SmCo}_{5-x}\text{Cu}_x$. *J. Less Common Met.* **34**, 285–291. [https://doi.org/10.1016/0022-5088\(74\)90171-4](https://doi.org/10.1016/0022-5088(74)90171-4) (1974).
17. Gabay, A. M., Larson, P., Mazi, I. I. & Hadjipanayis, G. C. Magnetic states and structural transformations in $\text{Sm}(\text{Co}, \text{Cu})_5$ and $\text{Sm}(\text{Co}, \text{Fe}, \text{Cu})_5$ permanent magnets. *J. Phys. D Appl. Phys.* **38**, 1337–1341. <https://doi.org/10.1088/0022-3727/38/9/002> (2005).
18. Suresh, K. *et al.* Coercivity of $\text{Sm}(\text{Co}_{0.9}\text{Cu}_{0.1})_{4.8}$ melt-spun ribbons. *J. Alloys Compd.* **436**, 358–363. <https://doi.org/10.1016/j.jallcom.2006.07.052> (2007).
19. Zhenhui, M. *et al.* A flame-reaction method for the large-scale synthesis of high-performance Sm_xCo_y nanomagnets. *Angew. Chem. Int. Ed.* **58**, 4509–4512. <https://doi.org/10.1002/anie.201907763> (2019).
20. Zhenhui, M., Ming, Y., Qiong, W., Chenglin, L. & Yongsheng, Y. Designing shape anisotropic SmCo_5 particles by chemical synthesis to reveal the morphological evolution mechanism. *Nanoscale* **10**, 10377–10382. <https://doi.org/10.1039/C8NR02893A> (2018).
21. Zhenhui, M. *et al.* Stabilizing hard magnetic SmCo_5 nanoparticles by N-doped graphitic carbon layer. *J. Am. Chem. Soc.* **142**, 8440–8446. <https://doi.org/10.1021/jacs.0c02197> (2020).
22. Xu, Y. H. *et al.* Chemically synthesizing exchange-coupled $\text{SmCo}_5/\text{Sm}_2\text{Co}_{17}$ nanocomposites. *Rare Met.* **40**, 575–581. <https://doi.org/10.1007/s12598-020-01516-z> (2021).
23. Haider, S. K., Lee, J. Y., Kim, D. S. & Kang, Y. S. Eco-friendly facile three-step recycling method of $(\text{Nd-RE})_2\text{Fe}_{14}\text{B}$ magnet sludge and enhancement of $(\text{BH})_{\text{max}}$ by ball milling in ethanol. *ACS Sustain. Chem. Eng.* **8**, 8156–8163. <https://doi.org/10.1021/acssuschemeng.0c00584> (2020).
24. Galkin, V., Haider, K., Ahn, J. B. & Kim, D. S. Effect of high energy ball milling washing process on properties of $\text{Nd}_2\text{Fe}_{14}\text{B}$ particles obtained by reduction-diffusion. *Key Eng. Mater.* **822**, 244–251. <https://doi.org/10.4028/www.scientific.net/KEM.822.244> (2019).
25. Suzuki, A. *et al.* Structure and magnetic properties of SmCo_{5-x} ($x=\text{Fe}, \text{Fe-Co}, \text{Co}$) magnetic bilayer films on MgO (110) substrate. *J. Magn. Magn. Mater.* **440**, 74–78. <https://doi.org/10.1016/j.jmmm.2016.12.061> (2017).
26. Shen, B. *et al.* A new strategy to synthesize anisotropic SmCo_5 nanomagnets. *Nanoscale* **10**, 8735. <https://doi.org/10.1039/C8NR01690A> (2018).
27. Boris, V. L. Mechanism of carbothermal reduction of iron, cobalt, nickel and copper oxides. *Thermochim. Acta* **360**, 109–120. [https://doi.org/10.1016/S0040-6031\(00\)00540-2](https://doi.org/10.1016/S0040-6031(00)00540-2) (2000).
28. Cheng, W. *et al.* Magnetic moments in SmCo_5 and $\text{SmCo}_{5-x}\text{Cu}_x$ films. *J. Supercond. Novel Magn.* **25**, 1947–1950. <https://doi.org/10.1007/s10948-012-1530-4> (2012).
29. Sinha, S. *et al.* On the evolving nature of c/a ratio in a hexagonal close-packed epsilon martensite phase in transformative high entropy alloys. *Sci. Rep.* **9**, 13185. <https://doi.org/10.1038/s41598-019-49904-5> (2019).
30. Zhang, C. W., Li, H., Dong, J. M., Guo, Y. Q. & Li, W. Electronic structure and magnetic properties of $\text{SmCo}_{5.85}\text{Si}_{0.90}$ alloy. *Phys. B.* **387**, 18–24. <https://doi.org/10.1016/j.physb.2006.03.017> (2007).
31. Yin, S. Q., Wang, H., Zhao, B., Jiang, Y. & Wang, J. P. The effects of Cu doping on crystalline structure and magnetic properties of $\text{SmCo}_{5-x}\text{Cu}_x$ thin films grown on Ru (0002). *J. Appl. Phys.* **114**, 213908. <https://doi.org/10.1063/1.4833558> (2013).
32. Chuev, M. A. Generalized Stoner–Wohlfarth model and the non-Langevin magnetism of single-domain particles. *JETP Lett.* **85**, 611–616. <https://doi.org/10.1134/S0021364007120053> (2007).
33. Chen, C. H. *et al.* The effect of particle size on coercivity and crystallinity of SmCo_5 . *Appl. Phys. Lett.* **99**, 012504. <https://doi.org/10.1063/1.3607958> (2011).

Acknowledgements

This work was supported by the Leader Project at the Sogang University funded by the Ministry of Science and ICT through the National Research Foundation of Korea (No. 2020R1A3B3079715). Y.S. Kang also appreciate the experimental support of National Research Council of Science and Technology (NST) grant by the Korea government (MSIT) (No.CRC-15-06-KIGAM).

Author contributions

S.K.H. did the experimental work, did characterization and wrote the manuscript. K.D. helped in the characterization and data analysis while H.N. helped in making figures. Y.S.K. helped in designing the experiment, worked on the basic ideas, helped in data interpretation and manuscript writing.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1038/s41598-021-89331-z>.

Correspondence and requests for materials should be addressed to Y.S.K.

Reprints and permissions information is available at www.nature.com/reprints.

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

© The Author(s) 2021