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 Ngo$^4$, Dongsoo Kim$^{2,3}$ & Young Soo Kang$^{1,2}$

SmCo$_5$ and SmCo$_{5-x}$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$_5$ ($12.86$ μB) to SmCo$_4$Cu ($10.58$ μB) and SmCo$_3$Cu$_2$ ($7.79$ μB) and enhanced anisotropy energy from SmCo$_5$ (10.87 Mega erg/cm$^3$) to SmCo$_4$Cu (14.05 Mega erg/cm$^3$) and SmCo$_3$Cu$_2$ (14.78 Mega erg/cm$^3$). Enhancement of the anisotropy energy increased the coercivity as its values for SmCo$_5$, SmCo$_4$Cu and SmCo$_3$Cu$_2$ 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$_3$Cu$_2$ 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$_3$Cu$_2$. 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 $1.19 \times 10^6$ erg/cm$^3$ 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$_s$ values$^{12}$. Decrease in the M$_r$ is the serious disadvantage that reduces the energy density/BH$_{\text{max}}$ 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 methods$^{13}$. 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$_5$Cu$_x$) decreases the price of the magnet produced, only up to 2%. Another important factor that may reduce the price of the SmCo$_3$Cu$_2$ 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$_3$Cu$_2$. 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$_3$Cu$_2$ could be reduced up to 6%. Reduced price of the SmCo$_5$

$^1$Department of Chemistry, Sogang University, 35, Baekbeomro, Mapoqu, Seoul 04107, South Korea. $^2$Powder and Ceramics Division, Korea Institute of Materials Science, Changwon, Gyeongnam 51508, South Korea. $^3$Convergence Research Center for Development of Mineral Resources, Korea Institute of Geoscience and Mineral Resources, Daejeon 34132, South Korea. $^2$Email: yskang@sogang.ac.kr
in this work may have a large impact, because global market value of the SmCo5 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. annealed Sm, Co and Cu for 304 h (21 days) at 1000 °C. Nishida et al. performed the annealing at more than 800 °C for 160 h. Gabay et al. annealed the Sm, Co and Cu for 100 h (50 h at 1050 °C then 50 h 350–450 °C). 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 homogenization. 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.

This study suggests an eco-friendly chemical method for the synthesis of the Cu substituted SmCo5 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 SmCo5 is reduced by substitution of Cu with Co. Extra added Co also increased the weight of SmCo5−xCux magnet which further reduced its cost.

Experimental section

Materials. Samarium chloride (SmCl3·6H2O, 99% purity), cobalt chloride (CoCl2·6H2O), copper chloride (CuCl2·2H2O, 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 SmCo5 and SmCo5−xCu 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. SmCl3·6H2O, CoCl2·6H2O and CuCl2·2H2O 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 SmCo5, Sm:Co molar ratio was kept as 1:4.2. Hence, 2.379 g of CoCl2·6H2O and 0.870 g of SmCl3·6H2O 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 SmCo4Cu and SmCo5−xCux, Sm:Co:Cu molar ratios were kept as 1:3.36:0.84 and 1:2.52:1.68 respectively. 15% extra Co was added to the SmCo5−xCux samples with Sm:Co:Cu molar ratio. SmCo5−xCux magnet which further reduced its cost. Co. Cost of the SmCo5 is reduced by substitution of Cu with Co. Extra added Co also increased the weight of SmCo5−xCu magnet which further reduced its cost.

Characterization. Crystal structure analysis was done with X-ray diffractometer (Rigaku MiniFlex) with Cu-Ka source radiation wavelength of 0.15418 nm. EDX, TEM, and HRTEM characterizations were done on JEM-2100F by JEOL Ltd. For these characterizations SmCo5 and SmCo5−xCu 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 SmCo5 and SmCo5−xCu products were measured by Physical Property Measurement System (PPMS, Evercool II–9T) in the vibrating sample magnetometer mode.

Results and discussion

SmCo5 and SmCo5−xCu particles were produced by the experimental process described in the experimental section. XRD patterns for all SmCo5 and SmCo5−xCu 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 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 structure of these products. Hence SmCo5−xCu particles are formed earlier (as compared to the SmCo5). Hence SmCo5−xCu particles are formed earlier (as compared to the SmCo5) and stay for
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 SmCo5−xCux particles as shown in EDX mapping image of Fig. 2 that indicates the complete formation of SmCo5−xCux 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 SmCo5−xCux/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.
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). Hence Cu reduces and diffuses much faster than Co and all Cu becomes the part of the SmCo5−xCux 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 SmCo5, with the similar atomic distribution found in CaCu5 type crystals. Co always occupies “3g” layer. “2c” layer is shared among Co and Sm, where Sm are on the edges of the SmCo5 crystal and Co is located between the Sm atoms. Cu substitutes the Co in “2c” layer (Fig. 3e) and enhances the magneto-crystalline anisotropy. Instability of Cu substitution at 3g sites is also confirmed by previous studies. Cu substitution has been clearly explained (Fig. 4) with top and side view of arrangement of the atoms in SmCo5 and SmCo5−xCux.

Enhancement in the crystal parameters “a, b, c” and crystal volume was recorded after substitution. SmCo5 and SmCo5−xCux 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.

\[
\frac{1}{d_{hkl}}^2_{hcpp} = \frac{4}{3} \left( \frac{h^2 + k^2}{a_{hcpp}^2} \right) + \frac{l^2}{c_{hcpp}^2}
\]

“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.
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% (SmCo4Cu) and 5% (SmCo3Cu2) as shown in the Fig. 4. Collectively, all the crystal parameters were increased after the substitution.

With electronic configuration of [Xe] 4f6 6s2, 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 SmCo5 is [Xe] 5d6 6s2 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 [Ar] 3d7 4s2 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 3d10 4s1 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 valence electrons make a valence band. This valence 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. SmCo5, Cu or SmCo3Cu2 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 $M_r$ 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 SmCo5. Measured magnetic hysteresis curves for the SmCo5, SmCo4Cu and SmCo3Cu2 are shown in Fig. 6b. The magnetic moment of SmCo5, SmCo4Cu and SmCo3Cu2 are to be 12.86, 10.58 and 7.79 $\mu_B$, respectively. In our work magnetic moment for SmCo5 and SmCo3Cu2 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 SmCo5 and SmCo3Cu2 are shown in Fig. 6b.

Reduction in magnetic moment critically affected on the anisotropy energy and coercivity. Coercivity (Hc) values of SmCo5, SmCo4Cu and SmCo3Cu2 were recorded as 4.5, 5.97 and 6.99 kOe, respectively. The increasing
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 $\text{SmCo}_5$, $\text{SmCo}_4\text{Cu}$ and $\text{SmCo}_3\text{Cu}_2$ were recorded as 10.87, 14.05, and 14.78 M erg/cm$^3$ 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 $\text{SmCo}_5-x\text{Cu}$ is also explained in the supplementary information.

Role of the extra Co phase present in the $\text{SmCo}_5-x\text{Cu}$ is very important. Cu enhances the coercivity at the cost of magnetic moment. Formation of $\text{SmCo}_3\text{Cu}_2$ after the substitution of Cu in $\text{SmCo}_5$ 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 $\text{SmCo}_3\text{Cu}_2$ is explained in Fig. S-9.

Coercivity of the $\text{SmCo}_5$ particles produced by chemical method is quite low as compared to the $\text{SmCo}_5$ 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)$^{12,13}$. In our work, particles with the similar size (average size 300 nm) were also separated and they exhibited much better magnetic

Figure 4. (a) Top and side view of arrangement of the atoms in $\text{SmCo}_5$ and $\text{SmCo}_5-x\text{Cu}$, (b) space-filling model of $\text{SmCo}_5$ and $\text{SmCo}_5-x\text{Cu}$ with crystal dimensions, (c) crystal parameters of $\text{SmCo}_5$ and $\text{SmCo}_5-x\text{Cu}$. 

![Image of arrangement of atoms and crystal parameters](https://example.com/image.png)
properties. Coercivity of SmCo$_3$Cu$_2$ was recorded as 13.5 kOe. Detail of this experiment and results obtained is described in the supplementary information.

**Conclusion**

SmCo$_5$ and SmCo$_{5-x}$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 SmCo$_{5-x}$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 SmCo$_{5-x}$Cu$_x$ up to 5%.
Figure 6. (a) Mechanism on the reduction of exchange coupling before and after Cu substitution in SmCo₅ and SmCo₅₋ₓCuₓ. (b) Magnetic hysteresis loops of SmCo₅ and SmCo₅₋ₓCuₓ. Variation of magnetic moment, Hc, Mr, Ms and anisotropy energy, before and after Cu substitution.

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

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