Synthesis of Samarium Cobalt Nanoblades

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Abstract

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As new portable particle acceleration technologies become feasible the need for small high performance permanent magnets becomes critical. With particle accelerating cavities of a few microns, the photonic crystal fiber (PCF) candidate demands magnets of comparable size. To address this need, samarium cobalt (SmCo) nanoblades were attempted to be synthesized using the polyol process. Since it is preferable to have blades of 1-2 μm in length, key parameters affecting size and morphology including method of stirring, reaction temperature, reaction time and addition of hydroxide were examined. Nanoparticles consisting of 70-200 nm spherical clusters with a 3-5 nm polyvinylpyrrolidone (PVP) coating were synthesized at 285°C and found to be ferromagnetic. Nanoblades of 25nm in length were observed at the surface of the nanoclusters and appeared to suggest agglomeration was occurring even with PVP employed. Morphology and size were characterized using a transmission electron microscope (TEM). Powder X-Ray Diffraction (XRD) analysis was conducted to determine composition but no supportive evidence for any particular SmCo phase has yet been observed.

Introduction:

i. Demand and Applications of Nano-scale Magnets.

As modern science and technology progress proceeds through the 21st century, material scientists and engineers will continue to create and take nanotechnology to unimaginable limits. One interesting aspect of nanotechnology is the use of nano-scale permanent magnetic materials. Applications range from high density magnetic recording devices to MRI contrast agents. Magnetic nanoparticles are even being used in Germany as part of an experimental tumor destroying procedure known as magnetic hyperthermia [1]. A very recent suggestion made by Dr. James Spencer of SLAC National Accelerator Laboratory, is to employ magnetic nanoparticles in a future particle accelerator concept based on PCFs.

ii. The involvement of Magnets in Particle Accelerators.

The very basis for magnets to be employed in particle accelerators goes back to the 19th century in the theory of electricity and magnetism. One of the most important results based on experiment is known as the Lorentz force and is given by,

$$\mathbf{F} = q (\mathbf{E} + \mathbf{v} \times \mathbf{B}). \quad (1)$$

The second term of this equation says that the magnetic force will be orthogonal to both the velocity of the particle and the magnetic field it interacts with. This implies that if one can create just the right configuration of magnets, one can establish a magnetic field that will influence the trajectory of a charged particle beam in just the way one desires. For example, a linear accelerator requires a series of focusing and defocusing magnets that will keep an electron or positron beam from diverging and interacting with the accelerating cavity's walls. A circular accelerator requires bending magnets which direct

particles into circular motion. Finally, a free electron laser which utilizes a linear accelerator requires a series of alternating dipole magnets known as an undulator to oscillate an electron beam to produce intense coherent photon beams.

iii. A Future Linear Accelerator Based on PCFs.

The traditional linear accelerator employs long copper cavities and RF power to accelerate electrons and positrons with a gradient of 25 MeV/m. Based on this number, the SLAC LINAC at 3000 m can boost electrons and positrons to a maximum energy of 75 GeV. In order to make new discoveries in high energy physics, this number must be inflated upto a TeV, where one TeV = 10^3 GeV. With this said, a 1 TeV linear accelerator based on copper RF cavities must be 40 km long. At this size economic feasibility becomes a real draw back. Accelerator physicists have devised new approaches to reaching higher energies, including the use of PCFs as an accelerating structure. A PCF is a silicon or silica optical fiber with an artificially constructed periodic array of vacuum defects that utilizes a photonic band gap to propagate specific frequencies of radiation. It has high potential as an accelerating structure as it was calculated by Eddie Lin that such a structure could produce an accelerating gradient of 0.38 GeV/m, which is more than 15 times larger than that of SLAC's LINAC [2]. With an acceleration cavity of a few microns, it is desirable to have the previously mentioned magnetic requirements of particle accelerators brought down to the same scale in order for PCF accelerators to become a reality.

iv. Samarium Cobalt Nanoblades.

A possible solution to the previous problem appeared in the summer of 2008 as researchers from Northeastern University and Sandia National Laboratory published a

paper proposing a new chemical method for producing samarium cobalt nanoblades of 100 nm by 10 nm dimension and values of the intrinsic coercivity and magnetization of 6.1 kOe and 40 emu/g and 8.5 kOe and 44 emu/g, at room temperature and 10 K, respectively [3]. The nanoparticle synthesis employed is commonly referred to as the polyol process.

v. The Polyol Process.

The polyol process is a chemical process which allows for the production of nanoparticles of a narrow size distribution. This occurs through the control of several parameters, most importantly, reaction time, reaction temperature, heating rate, and surfactant to ion concentration. The process involves the classic redox reaction, where redox is short for reduction-oxidation. This refers to the ability of two chemically distinct species to transform as one species gains electrons and the other loses electrons. In the polyol process, a solvent is chosen which also acts as the reducing agent by reducing dissolved metal cations into metal atoms as it itself is being reduced. The reaction mechanism for formation of SmCo particles involves an initial reduction of Co^{2+} to Co and the creation of amorphous Sm_2O_3 as an intermediate both of which involving tetraethylene glycol (TrEG). The intermediate Sm_2O_3 phase favors a rapid generation of dissolved Co species that are finally reduced to form crystalline SmCo particles [3]. A reaction scheme can be seen in **Scheme 1**. Once SmCo particles form in nuclei, crystal growth is regulated by the interaction between the metal particles and surfactant. In the paper, polyvinylpyrrolidone (PVP) was employed. Its carbonyl group interacts with the charge distribution at the metal surface resulting in a shift in electron density and electrostatic attraction due to the high electronegativity of the carbonyl oxygen. This

results in an organic coating of the metal nanoparticles which may function to keep particles from aggregating through steric hindrance (electrostatic repulsion) and to protect from oxidation as nanoparticles are extremely prone to reaction with oxygen gas due to their large surface area to volume ratio [4]. Molecular structures of TrEG and the basic unit of PVP may be seen in **Figure 1**.

vi. Samarium Cobalt Physical Properties.

Samarium cobalt is a binary compound that exists as a metal alloy with many phases as seen in the phase diagram found in **Figure 2** [5]. SmCo alloy is a rare-earth-transition-metal (RE-TM) permanent magnetic material, which is characterized by having a sufficiently high Curie temperature, a high remanent magnetization, and a high magnetocrystalline anisotropy [3], [5]. The first two of these properties are provided predominantly by the sublattice of the 3d element cobalt, while the third is due mainly to the rare-earth samarium, sublattice [5]. The high Curie temperature allows for the material to remain in a ferromagnetic phase, hence remain spontaneously magnetized which is important for the integration into a particle accelerator. The high remanence magnetization allows for the construction of strong enough magnetic fields to adequately influence charged particle beams in a desired fashion. Finally, the high magnetocrystalline anisotropy helps prevent domain reversal by establishing a crystal easy axis, hence allowing for a better preservation of magnetization. The domains will energetically favor preserving the anisotropy even when external fields are applied, thus particularly dominant anisotropic phases, 1:5 and 2:17, will tend to be present each with a high intrinsic coercivity [6]. The 2:17 phase exhibits higher magnetic performance at the

cost of having a more complex lattice structure. Unit cells for each of these phases are found in **Figure 2** [5].

vii. Experimental Purpose.

In order to implement samarium cobalt magnets into PCFs for accelerator design, they must first be created to the desired scale. Since there is no easy way to synthesize blade-like particles of microns in length, the previously proposed method was attempted to be reproduced with emphasis on the influences of stirring method, reaction temperature, reaction time and addition of sodium hydroxide in optimization of nanoparticle creation and size. The influence of key parameters on magnetic properties would also be critical and would be a later extension of this work. For the 1:5 phase, it can be estimated that the maximum size of a monodomain particle is given by,

$$d_c = 18\gamma/\mu_0 M_s^2 = 2 \mu\text{m}, \quad (2)$$

where γ is the domain wall energy per unit area and M_s is the saturation magnetization [7]. Based on this approximation and the PCF cavity size, a narrow size distribution within the 1-2 μm size range of 1:5 phase crystallites would be ideal once a basis of understanding the synthesis process is established.

Methods:

i. Safety Considerations.

When working in a wet chemical lab it is imperative to wear proper personal protection equipment (PPE). For the purposes of this experiment, nitrile gloves, complete coverage safety goggles and a lab coat have been worn and maintained at the experimental site. MSDS information reported that none of the required chemicals have

serious acute toxicity concerns or carcinogenic effects; however cobalt containing compounds are known to be toxic in large doses. Review **Table 1** for experimental hazard descriptions and hazard controls.

ii. Chemicals and Apparatus.

99.9% purity samarium (III) nitrate hexahydrate, 98% purity cobalt (II) nitrate hexahydrate, 99% purity tetraethylene glycol, polyvinylpyrrolidone (PVP, molecular weight = 55k), ethanol and hexane were obtained from Sigma Aldrich. A series of syntheses were conducted at the Geballe Laboratory of Advanced Materials (GLAM) at Stanford University. The syntheses deviated from the original published work by being conducted using a Schlenk line technique as opposed to the more laborious glove box method. A typical double manifold Schlenk line may be seen in **Figure 3** [8]. Please consult references [9] and [10] for more information on Schlenk line procedural details.

iii. Characterization Instrumentation.

Optical microscopy was performed using an Olympus SZX9 camera. TEM imaging was conducted on a FEI TECNAI TEM using a copper grid for sample placement. XRD was done using a PANalytic X'Pert PRO instrument with a copper target. Both instruments were used at the Stanford University Nanocharacterization Laboratory (SNL).

iv. Synthesis 1: Magnetic Stir Bar Method.

2.2 mg $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 7.3 mg $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and 564 mg PVP (55k) were dissolved in 15 ml TrEG in a 25 ml three-necked, round-bottom flask that contained a half inch magnetic stirring bar. The central neck of the flask was connected to a condenser and attached to the apparatus. The flask was supported underneath by a heating

mantle which rested on an elevated magnetic stirring plate. A rubber septum was placed on one side neck and a thermocouple attached to the other. The reaction vessel was evacuated for 15 min at room temperature and then for 30 minutes at 100°C. The solution became a pink color due to the dissolved $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The vessel was then filled with nitrogen gas at 4 psi and heated to 200°C for one hour. Color changes were rather quick from pink, to orange, to red, to merlot and finally to black. After one hour of heating the reaction vessel was cooled to room temp, the magnetic stir bar removed and the solution centrifuged for 15 minutes at 6500 rpm to reveal no noticeable product. The magnetic stir bar was then looked at under an optical microscope.

v. Synthesis 2: Nitrogenation Method.

3.3 mg $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 10.5 mg $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 554 mg PVP (55k) were dissolved in 15 ml TrEG in a 25 ml three-necked, round-bottom flask. A septum was added to one side neck and a thermocouple to the other. No magnetic stir bar was present. The reaction vessel was evacuated for the same duration as synthesis 1. Prior to switching to nitrogen, a 16 gauge trans-spinal needle connected to a nitrogen gas source was injected through the septum. The vacuum was switched to nitrogen followed by turning on of the additional nitrogen bubbling source. Heating was conducted at 200°C for one hour with the same color changes observed. The final black solution was centrifuged at 7500 for 15 min after adding ethanol with no observable product.

vi. Synthesis 3: Magnetic Stir Bar Method with SmCo_5 Magnet.

13 mg $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 42 mg $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 2.22 g PVP (55k) were dissolved in 60 ml TrEG in a custom three-necked flask after adding an approximately inch and a half SmCo_5 permanent bar magnet was wrapped in teflon except for a small portion at the

center of the easy axis face. The vessel was evacuated for 15 minutes at room temperature followed by 30 minutes at 100°C. Once vacuum was switched to nitrogen, the vessel was heated to 200°C and sat there for one hour. After the vessel was cooled similar processes were conducted with solution to reveal no noticeable product.

vii. Synthesis 4: Nitrogenation at Elevated Temperature.

3.2 mg $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 10.0 mg $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 550 mg PVP (55k) were dissolved in 15 ml TrEG in a 25 ml three-necked, round-bottom flask with no magnetic stirring bar. Vacuum procedures followed synthesis two and the same 16 gauge trans-spinal needle was injected through septum following switch from vacuum to nitrogen just as synthesis 2. The flask was wrapped in aluminum foil and heated to 290°C and allowed to sit for one hour after stabilizing at that temperature. A dark black solution was observed. After adding hexane to solution, centrifugation at 8000 rpm for 30 min resulted in the observation of a dark black powder that was dispersed in ethanol. TEM images were taken as will be discussed in the data section.

viii. Synthesis 5: Nitrogenation at Elevated Temperature for a Longer Time.

43.0 mg $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 134 mg $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 7.33 g PVP (55k) were dissolved in 200 ml TrEG in a 250 ml three-necked, round-bottom flask. The vessel was evacuated for 30 min at room temperature and 45 min at 100°C. After switching to nitrogen and adding the bubbling needle, the flask was covered in aluminum foil and the solution was heated at a rate of 7.5-9.0°C/min for 1.25 hrs until 285°C was reached. The solution was stabilized at 285°C for 1.5 hrs, then allowed to cool to room temperature for 1 hr. Removal of the foil revealed a dark black solution. Following the same centrifugation procedure as synthesis 4, a darker black powder was recovered and

dispersed in ethanol. XRD and TEM techniques were used to characterize particles as will be discussed.

ix. Synthesis 6: Addition of Sodium Hydroxide.

7.3 mg $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 20.1 mg $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 19.3 mg NaOH and 1.10 g PVP (55k) were dissolved in 30 ml TrEG in a 50 ml three-necked round-bottom flask. The vessel was evacuated for 15 min at room temperature, 10 min at 50°C and 15 min at 100°C. At 85°C, the initial pink solution changed to a light yellow-green then to gold. The vacuum was switched to nitrogen and a 16 gauge trans-spinal needle was injected for nitrogenation. The solution was heated slowly for 1 hr till it reached 285°C. Once stabilized, the solution was stirred and maintained at 285°C for 2 hrs. The solution was cooled to 50°C for 30 min and centrifuged at 8000 rpm for 30 min after adding toluene to yield a black powder product. The powder was rinsed several times and dispersed in ethanol. XRD and TEM characterization is in progress.

Results:

Optical microscope imaging of the magnetic stir bar of synthesis 1 revealed what appears to be reflective metallic circular structures on the surface as can be seen in **Figure 4**. Synthesis 2 produced no noticeable product. Synthesis 3 may have produced similar light depositing as the teflon coated stir bar synthesis 1, but no significant crystal growth was observed. Synthesis 4 produced 70 nm polycrystalline nanoclusters as can be seen in **Figure 5**. A PVP coating of 3-5 nm was observed in **Figure 6**. Synthesis 5 produced 150-200 nm polycrystalline nanoclusters as can be seen in **Figure 7**. Nanoblades of 25 nm were clearly differentiated and appeared amongst the nanoclusters as can be seen in **Figure 8**. An XRD spectrum was taken but is not reported as it did not

match a single SmCo or Co phase. When dispersed in ethanol the particles produced in synthesis 6 have a similar optical density and settling behavior as the nanoclusters from syntheses 4 and 5 suggesting agglomeration once again. XRD and TEM characterization have not yet been conducted.

Discussion and Conclusion:

i. Stirring method.

The results of syntheses one and three reveal that the use of conventional magnetic stirring is ineffective for producing nanoscale particles capable of being dispersed at least at a reaction temperature of 200°C. Further investigation on the effects of magnetic stirring at varying temperature would need to be conducted in order to be effective. It does ask the question of whether metal structures may be grown uniformly off a magnetic substrate, which would also require further investigation. The use of a stainless steel needle allowed for stirring through nitrogenation and proved a successful method although the effect of nitrogen flow rate on particle size and morphology is unknown. It seems clear that adequate stirring that perturbs or prevents the settling out of the heavy metal alloy should improve the size and rate of crystal growth.

ii. Reaction temperature.

It is clear that a reaction temperature of 285-290°C which is close to the boiling point of TrEG is preferable for efficiently producing nanoparticles as the products of syntheses 4-6 indicate. A direct study of reaction temperature and particle size distribution at constant reaction time is a future possibility for reaction temperature optimization.

iii. Reaction time.

From the TEM images of the products of Syntheses 4 and 5, it is apparent that a longer reaction time resulted in a doubling of particle size. Reaction time could be optimized with further study in conjunction with more optimal methods.

iv. Sodium Hydroxide Addition.

Characterization of the product of Synthesis 6 is currently being done.

v. Other Findings.

The near transparent coating seen in the TEM images at the nanocluster surfaces suggests PVP has successfully coated the metal particles which may prevent oxidation but may impede crystal growth. The different shades within the particles suggests a polycrystalline composition, but there is no conclusive evidence yet to identify the products as SmCo or even Co and so further compositional analysis is necessary. It is possible that the coreduction was faulty which lead to addition of NaOH in Synthesis Six in order to help boost the kinetics of the Samarium ion reduction which is imperative to coalesce with the Cobalt ion reduction in order to successfully form SmCo nuclei. The products of Syntheses 4-6 were found to be ferromagnetic due to their attraction to a permanent magnet and it is unknown whether they are mono or poly domain. As apparent from the very formation of the nanoclusters, agglomeration is an issue preventing monodispersion of nanoblades, which will require greater investigation. Work on this project is to be continued over the course of the next several months at GLAM as well as at California State University, Sacramento and University of California at Davis.

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Figure 1: Structures of TrEG and PVP basic unit.

Scheme 2: Formation of SmCo through Polyol Process.

Figure 2: Samarium cobalt alloy phases. SmCo₅ is on the right.

Hazard	Hazard Description	Probability/Severity	Control	Hazard Risk with control implemented
Chemical exposure to skin	Irritation or chemical absorption through skin. Acute and chronic risks found in MSDS.	High probability of skin contact/ Low severity of direct external exposure.	Utilization of proper PPE. Nitrile gloves and lab coat. Store unused reagents in respective chemical cabinets and chemical waste in designated waste containers.	Very low.
Chemical exposure to eyes	Irritation or blindness. Specific descriptions found in MSDS.	Moderate probability of eye contact/ Moderate to high severity from eye contact	Utilization of proper PPE. Complete closure safety goggles.	Very low.
Chemical exposure by inhalation or ingestion	Specific effects depend on dose and given in MSDS. Chronic toxicity effects are noted but not fully evaluated for both metal nitrates.	Moderate probability/ Low to moderate severity	Dry chemicals and liquids should be handled in fume hood as much as possible, storage containers should be closed after use, and all spills should be cleaned up immediately.	Very low.
Direct exposure to liquid nitrogen	Contact of liquid nitrogen by skin or clothes may result in severe burns and permanent tissue damage.	Low probability/ Low to high severity depending on circumstance.	Store liquid nitrogen out of immediate work area in properly labeled dewar and utilize standard liquid nitrogen PPE including cryogenic gloves and safety goggles during transfer.	Moderately low.
Contact of heating mantle or hot glass	Moderate burns may result from contacting heated objects.	Low probability/ Low severity.	Maintain knowledge of where heated objects are located and allow hot glass to return to room temperature touching glass with back of hand prior to handling.	Very low.
Ignition of samarium cobalt alloy or tetraethylene glycol during reaction phase.	Heating up to 300°C provides conditions for combustion of SmCo metal and glycol vapor, if oxygen gas and an ignition source are present in reaction vessel.	Low probability/ Moderate severity	Allow for several vacuum-nitrogen cycles prior to heating. Close fume hood during reaction in the unlikely event that a systematic failure results in combustion. Ensure no flames or source of sparks are present in fume hood during reaction.	Moderately low.
Condensation of oxygen in Schenk line trap	Liquid oxygen is extremely dangerous and reacts violently with organic compounds. If it collects in trap and then evaporates, it may result in Schenk line manifold explosion.	Moderate probability/ Moderate to high severity depending on concentrations of organic compounds in cold trap.	When shutting down Schlenk line manifold, remove liquid nitrogen from trap and allow glass to return to room temperature prior to shutting off vacuum pump.	Very low.

Table 1: Experimental Hazards and Controls

Figure 3: Schlenk line double manifold apparatus.

Figure 4: Optical microscope image of the Teflon coated magnetic stir bar surface from synthesis 1. The metallic coating over the teflon is clearly evident.

Figure 5: TEM image of nanoclusters from synthesis 4.

Figure 6: TEM image of nanocluster surface showing PVP coating and polycrystalline composition.

Figure 7: TEM image of larger nanocluster from synthesis 5.

Figure 8: TEM image of nanoblades from surface of nanocluster.