Ferromagnetic Gd_5Si_4 Nanoparticles for Medical Applications

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ABSTRACT

Gadolinium nanoparticles are widely used as contrast agents for magnetic resonance imaging. Unfortunately, these commercially available gadolinium nanoparticles are paramagnetic at body temperature, limiting the signal to noise ratio of the imaging. Bulk samples of $Gd_5(Si_xGe_{1-x})_4$ have been studied and shown to have ferromagnetic properties, but nanoparticles of the material have not been previously reported. Iowa State University and Ames Laboratory researchers have developed a process to produce Gd_5Si_4 nanoparticles that retain ferromagnetic properites at room temperature.

Keywords: ferromagnetic, gadolinium, nanoparticle, MRI

1 INTRODUCTION

Medical applications for magnetic nanoparticles include both therapeutic and diagnositc applications [1]. Therapeutic applications include targeted drug delivery as well as hyperthermia, the localized heating of cells due to flipping of the magnetization direction of the particles in an alternating current magnetic field. The most broadly used diagnostic application is magnetic resonance imaging (MRI), which when combined with the use of contrast agents shows enhanced contrast between normal and diseased tissues and can indicate blood flow and organ function. MRI contrast agents are based on magnetic nanoparticles, many of which contain gadolinium. Commerical gadolinium-based contrast agents exhibit paramagnetic behavior at body temperature. Signal to noise ratios for these gadolinium-based contrast agents could be increased considerably if the nanoparticles instead exhibited ferromagnetic behavior at body temperature.

Iowa State University and Ames Laboratory researchers have synthesized ferromagnetic nanoparticles of Gd_5Si_4 by high energy ball milling. Milling times and intensity were investigated; prolonged milling time causes the loss of crystal structure and the resultant loss in long range ordering [2].

2 EXPERIMENTAL

Arc melting of a stoichiometric mixture of gadolinium and silicon was used to create the bulk polycrystalline samples of Gd_5Si_4. The sample was melted under an argon atmosphere, and was remelted six times to ensure homogeneity of the sample. No additional heat treatments were applied to the cast sample. The sample was then ground in an agate mortar to obtain powder with a nearly uniform particle size of 53 μm. Further size reduction was obtained by high energy ball milling in a SPEX 8000 M under an argon atmosphere. No liquid processing agent was utilized in the milling process.

2.1 Ball Milling

Typical procedures for milling are comprised of combining 4 g of bulk powder as described above with roughly 14.5 g of stainless steel balls. The stainless steel balls consisted of two balls of 11.1 mm diameter and four balls of 6.3mm diameter. For sample S2, the balls were replaced after twenty minutes of milling with forty balls of 2.9 mm diameter, after which milling continued for an additional twenty minutes.

Sample ID	Milling Time	Milling Balls (number of balls and diameter in mm)
S1	20 minutes	2x11.1 and 4x6.3
S2	40 minutes	2x11.1, 4x6.3 and 40x2.9
S3	24 hours	2x11.1 and 4x6.3
S4	72 hours	2x11.1 and 4x6.3

Table 1: Sample ID with Milling Time and Milling Ball Description.

2.2 Characterization

Particle size, morphology, crystal structure and magnetic properties were determined for both bulk and ball-milled samples. SEM photographs of the various samples, shown in Figure 1, show significant agglomeration of the particles in samples S2, S3 and S4. Non-agglomerated particle size ranged from 200 nm to 2 μm. Additonally there was a significant amount of contamination of metallic iron in samples S3 and S4 from the steel balls and container; no contamination was found in samples S1 and S2.

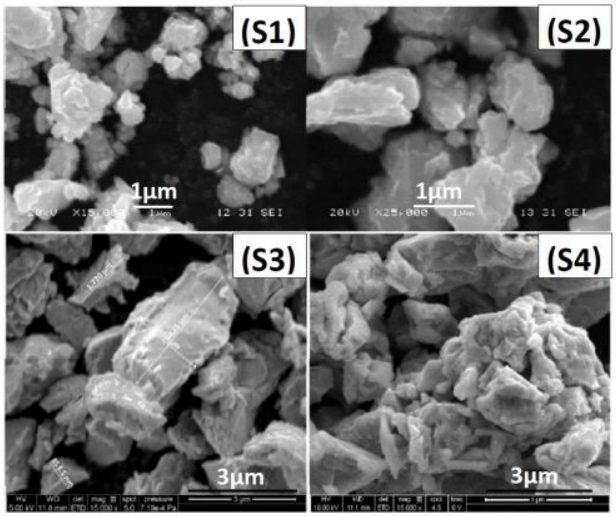

Figure 1: SEM images of Gd_5Si_4 particles showing agglomeration. Note that agglomeration increases with milling time. Taken from [2].

Figure 2 shows magnetization at an applied field of 100 Oe versus temperature for bulk Gd_5Si_4 and samples S1 and S2. Sample S1 retains a ferromagnetic transistion between 330-340 K, whereas S2, with a longer milling time, has two more pronounced transitions at 100 K and 280 K.

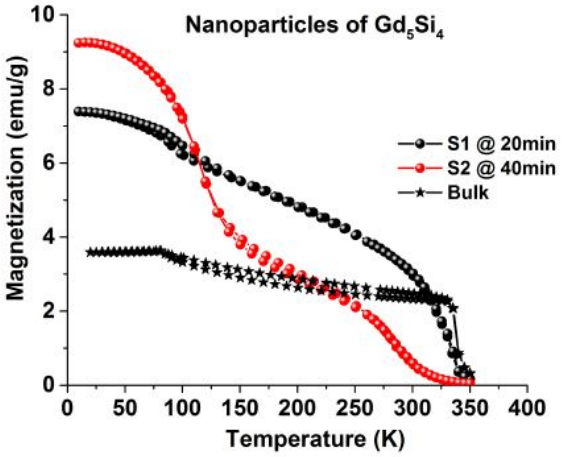

Figure 2: Magnetization versus temperature at an applied field of 100 Oe. Note the broadened phase transition for S2 as a result of increased milling time. Taken from [2].

Figure 3 shows magnetization as a function of magnetic field for S1 and S2 at varying temperatures. Both samples demonstrate ferromagnetic behavior at 275 K, while at 350K S2 is clearly paramagnetic and S1 is nearly so.

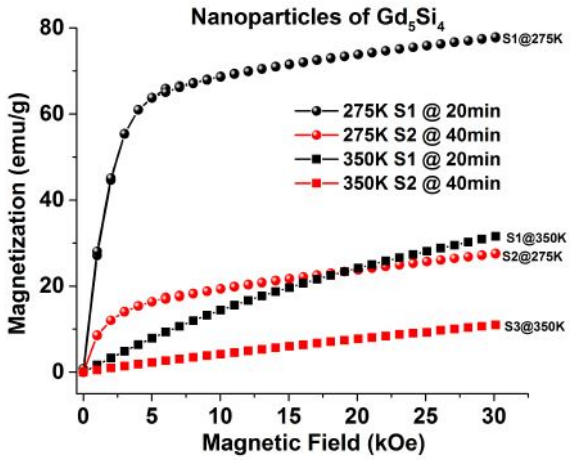

Figure 3: Magnetism versus magnetic field at 275 K and 350 K. Taken from [2].

Figure 4 shows hysteresis loops for samples S1 and S2; the inset shows details at low magnetic field strengths. Sample S2 has higher coercivity than S1 at 30 Oe, possibly due to pinning sites from longer milling of the material.

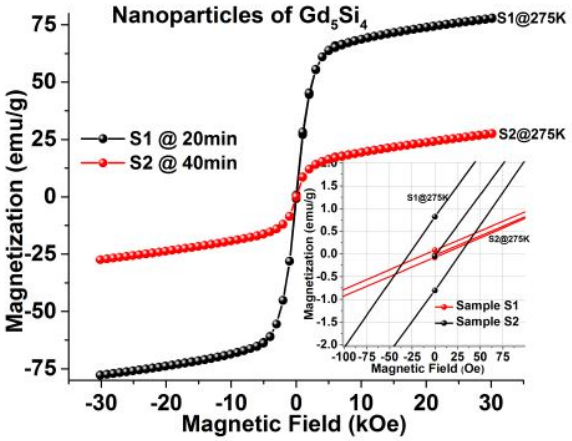

Figure 4: Hysteresis of samples S1 and S2 at 275 K. Taken from [2].

Finally, magnetization versus milling time is shown in Figure 5. Magnetizaton was measured at 275 K in a 10 kOe applied field. A marked decrease in magnetization occurs with increasing milling time, demonstrating the need for optimization of magnetization versus particle size distribution at milling times close to twenty minutes.

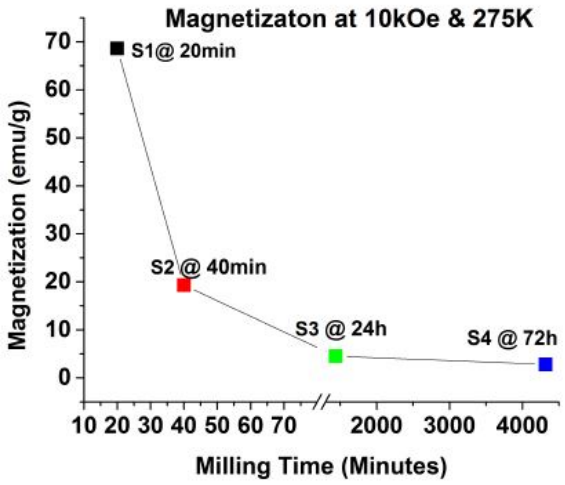

Figure 5: Magnetization versus milling time at 275 K and 10 kOe. Magnetization decreases significantly with increasing milling time. Taken from [2].

3 DISCUSSION

Nanoparticles of Gd_5Si_4 produced by short duration, high-energy ball milling retain crystallinity and the ferromagnetic transition of bulk Gd_5Si_4 at 340 K. While optimization of process conditions is still required, the results thus far indicate the possibility of making ferromagnetic particles suitable for use in medical applications.

REFERENCES

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