11-2015

Investigation of Room Temperature Ferromagnetic Nanoparticles of Gd5Si4

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Abstract
Gd5(SixGe1-x)4 compounds undergo first-order phase transitions close to room temperature when x ~ = 0.5, which are accompanied by extreme changes of properties. We report the fabrication of the nanoparticles of one of the parent compounds-Gd5Si4-using high-energy ball milling. Crystal structure, microstructure, and magnetic properties have been investigated. Particles agglomerate at long milling times, and the particles that are milled >20 min lose crystallinity and no longer undergo magnetic phase transition close to 340 K, which is present in a bulk material. The samples milled for >20 min exhibit a slightly increased coercivity. Magnetization at a high temperature of 275 K decreases with the increase in the milling time.

Keywords
room temperature ferromagnetic nanoparticles, magnetocaloric nanoparticles, Gadolinium nanoparticles, Contrast agents

Disciplines
Electrical and Computer Engineering | Metallurgy | Nanotechnology Fabrication

Comments
This is a manuscript of an article published as Hadimani, R. L., S. Gupta, S. M. Harstad, V. K. Pecharsky, and D. C. Jiles. "Investigation of Room Temperature Ferromagnetic Nanoparticles of Gd 5 Si 4." IEEE Transactions on Magnetics 51, no. 11 (2015): 1-4. DOI: 10.1109/TMAG.2015.2446774. Posted with permission.

This article has been accepted for publication in a future issue of this journal, but has not been fully edited. Content may change prior to final publication. Citation information: DOI 10.1109/TMAG.2015.2446774, IEEE Transactions on Magnetics

Investigation of room temperature ferromagnetic nanoparticles of Gd_5Si_4

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Abstract: $Gd_5(Si_xGe_{1-x})_4$ compounds undergo first order phase transitions close to room temperature when x ≅ 0.5, which are accompanied by extreme changes of properties. We report the fabrication of nanoparticles of one of the parent compounds – Gd_5Si_4 – using high energy ball milling. Crystal structure, microstructure and magnetic properties have been investigated. Particles agglomerate at long milling times and the particles that are milled longer than 20 min lose crystallinity and no longer undergo magnetic phase transition close to 340 K, which is present in a bulk material. Samples milled for more than 20 min exhibit a slightly increased coercivity. Magnetization at a high temperature of 275K decreases with increase in milling time.

***Index Terms*: room temperature ferromagnetic nanoparticles, magnetocaloric nanoparticles, Gadolinium nanoparticles, Contrast agents.**

I. Introduction

The $Gd_5(Si_xGe_{1-x})_4$ [x = 0–1] system has been widely studied in bulk form due to its interesting properties at the phase transition [1–5]. There are a few reports on the fabrication of thin films of this material [6–8] but, there are no reports in the literature on synthesis and characterization of nanoparticles of this material. Unlike films, which are expected to have low refrigeration capacity due to low volume, nanoparticles have the potential to overcome this problem if a scalable and cost-effective method of nanoparticle fabrication can be developed. Few articles have been published recently on the magnetocaloric effect of ferrites and non-rare earth particles which is below 1 J/kgK for a field change of 3 tesla [9-11]. Gadolinium nanoparticles are also widely used as contrast agents during magnetic resonance imaging (MRI) however, the particles are paramagnetic at body temperature. Signal to noise ratio can be significantly increased if we can synthesize gadolinium based nanoparticles that are ferromagnetic. In this work, we have synthesized ferromagnetic sub-micron particles of Gd_5Si_4 by high-energy ball-milling varying milling times and milling intensity. We have investigated their microstructure, crystal structure, composition and magnetic properties. We have determined the milling time beyond which the particles become non-crystalline and lose the long range ordering. We also show that the coercivity of the particles increases with increasing the milling time.

II. Experimental Details

Polycrystalline sample of Gd_5Si_4 was synthesized by arc-melting of the stoichiometric mixture of commercial grade Gd (purity generally quoted as 99.9 % by wt. with respect to other rare earths) and Si (Cerac Inc., USA, >99.999%) on a water-cooled Cu-hearth under argon atmosphere. The sample was re-melted six times turning over each time to ensure homogeneity. The last melting was finished by shutting off power to the arc allowing for the highest cooling rates in order to avoid the formation of neighboring phases. No further heat treatment was performed on the as-cast sample. This process usually leads to phase pure alloys [12]. Using commercial grade of Gd leads to the formation of a small amount of Gd_5Si_3 impurity in the predominantly Gd_5Si_4 matrix.

To obtain sub-micron of Gd_5Si_4, the as-cast bulk material was first ground in an agate mortar and sieved to obtain powder with nearly uniform particle size of 53 microns or smaller. Further reduction in the particle size was achieved by high-energy ball-milling of the powder in a SPEX 8000M mill without adding any liquid processing agent. In order to prevent surface oxidation, all millings and subsequent manipulations were performed in a glove box under argon atmosphere. In a typical milling procedure, 4 g of bulk powder was milled with approximately 14.5 g of stainless-steel balls consisting of 2 balls of 11.1 mm dia. and 4 balls of 6.3 mm dia. The powder was initially milled for 24 h at which point the milling was interrupted, and some sample (designated as S3) was withdrawn for analysis. The milling was then continued up to 72 h to obtain sample S4. Considering the significant contamination of these two samples with metallic iron from the steel balls and the container, a two step-milling

TABLE I
Sample ID with milling time and milling ball description

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, 4x6.3and 2.9x40
S3	24 hours	2x11.1 and 4x6.3
S4	72 hours	2x11.1 and 4x6.3

Manuscript received March 20, 2015. Corresponding author: R. L. Hadimani (e-mail: hadimani@iastate.edu).
Digital Object Identifier inserted by IEEE

This article has been accepted for publication in a future issue of this journal, but has not been fully edited. Content may change prior to final publication. Citation information: DOI 10.1109/TMAG.2015.2446774, IEEE Transactions on Magnetics

was utilized in which the milling time was reduced to 20 min at each step to limit contamination. During stage 1 of the process (sample S1), 4 g of bulk powder was milled for 20 min under same conditions as used for the previous two samples. In the second stage, 3 g of powder recovered from stage 1 was mixed with ~30 g of 2.9 mm stainless steel balls (~40), and milled for another 20 min (sample S2). Table 1 lists the samples IDs with milling time and milling ball description. The bulk and all the ball-milled samples were analyzed for their particle size, morphology, composition, crystal structure and magnetic properties using Scanning Electron Microscope (SEM), Energy Dispersive X-ray Spectroscopy (EDS), XRD (X-Ray Diffraction) with Co-source and step size of 0.001° and SQUID magnetometer, respectively. No further annealing of milled powders was performed before physical property measurements.

III. Results and Discussion

SEM micrographs showed that the particles were agglomerated significantly in S3, S4 and S2 samples while the agglomeration in S1 sample was not as pronounced as seen in Fig. 1. The size of particles that were not agglomerated varied from 200nm to 2 μm in all the samples. Composition analysis by EDS indicated presence of iron from milling media in samples S3 and S4. The volume fraction of iron was ≈30% and ≈44% in S3 and S4 samples respectively. Iron was not detected in S1 and S2 that have been milled for shorter duration and by milling in 2 *stages* with higher intensity in stage 2. Oxygen was not considered during the EDS analysis.

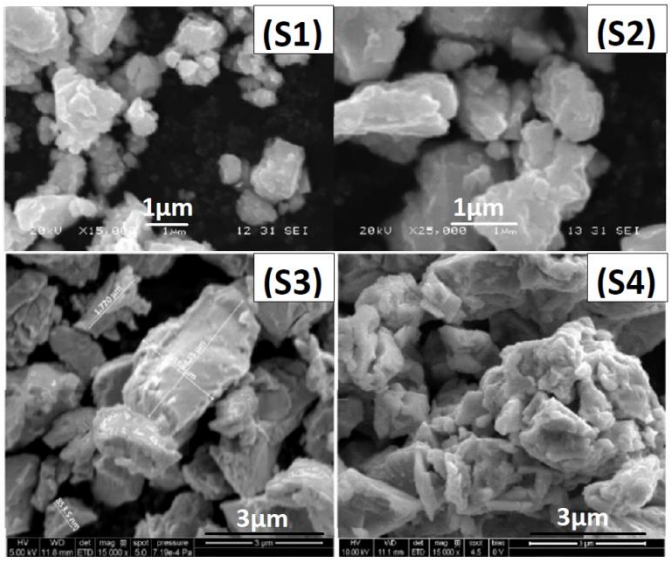

FIG. 1 SEM images of particles of Gd_5Si_4 showing agglomeration at all the stages of sample S1, S2, S3 and S4. Note that the agglomeration increases with milling time.

The samples were taken out from the glove box and exposed to atmosphere at the time of characterization. The particles may have been oxidized. Since Gd_2O_3 has transition temperature below 10 K [13], it will be non-magnetic at higher temperatures and small volume fraction of this phase will not affect the magnetic properties of Gd_5Si_4 particles. Fig. 2 shows XRD pattern for S1, S2, S3 and S4 samples. The X-ray patterns for S3 and S4 exhibit broad halos between 30 and 40° consistent with amorphous or nearly amorphous state. Bragg peaks corresponding to iron are also indistinguishable, indicating that iron particles are x-ray amorphous. Broad halos observed in the vicinity of 20° are from a polymer holder used to contain the particles. Sample S1 shows weak but narrow Bragg peaks between 30° and 40° which correspond to Gd_5Si_4.

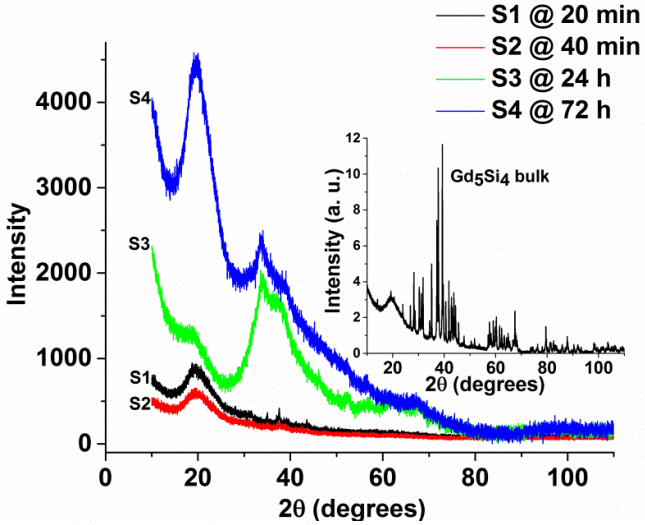

FIG. 2 XRD patterns for S1, S2, S3 and S4 samples under different milling conditions. Inset shows XRD peak patterns for bulk Gd_5Si_4.

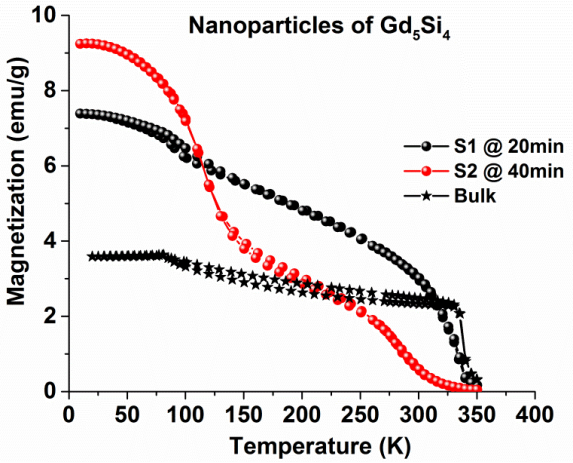

FIG. 3 Magnetization vs. Temperature at an applied field of 100 Oe for samples S1, S2 and bulk samples. The phase transition has broadened with milling time of the samples

When the milling is continued for up to 40 minutes with higher milling intensity in sample S2, the corresponding Bragg peaks start to disappear. Inset in Fig. 2 shows the XRD pattern of crystalline Gd_5Si_4. The particles loose crystallinity between milling times of 20 to 40 minutes and become amorphous. Since Fe was identified in EDS and not in XRD, it might be either present as amorphous particles or might be dissolved into the Gd_5Si_4 matrix. However, if it was present as amorphous particles, the back scattered images in SEM (CBS)

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would have shown different contrast which was not observed (CBS images not included in the manuscript). It may be possible that Fe might have dissolved into Gd_5Si_4 matrix but not formed as amorphous particles based on the back scattered images.

Fig. 3 shows magnetization as a function of temperature at an applied field of 100 Oe for S1, S2, and bulk Gd_5Si_4. As the milling time is increased in S2, the transition close to 340 K has disappeared and two ferromagnetic-like transitions are observed near 280 and 100 K. S1 retains a ferromagnetic transition at ~330-340 K, but it also exhibits a weak anomaly near 100 K which may be due to the presence of secondary phase of Gd5Si3 whose transition temperature is close to 100 K [14].

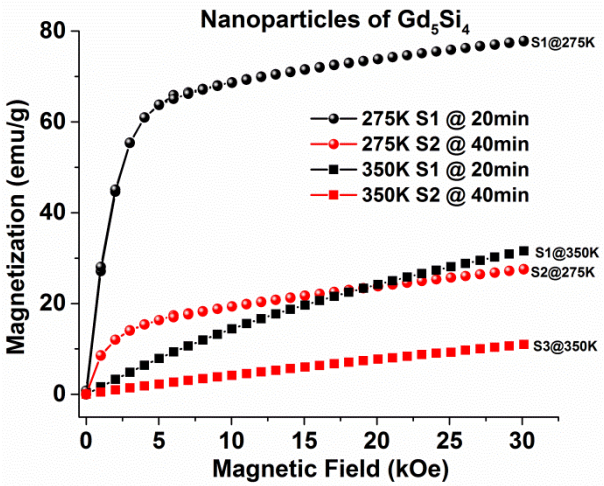

FIG. 4 M vs. H at 275 K and 350 K for samples S1 and S2. Note that the 350 isotherms in both the samples are paramagnetic indicating that there is no iron contamination from the milling media.

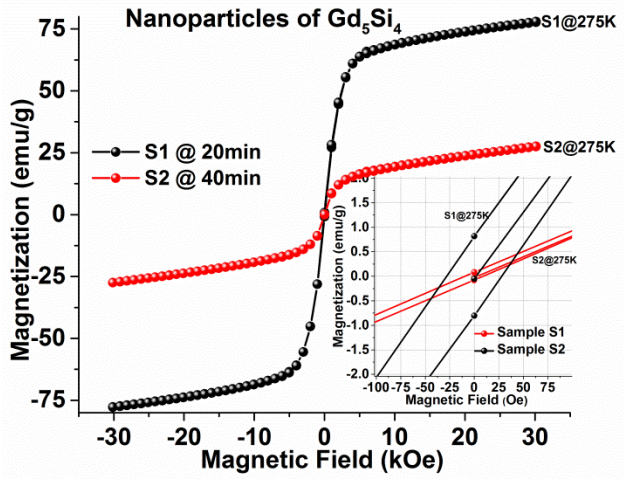

FIG. 5 Hysteresis of samples S1 and S2 measured at 275K.Coercivity of the samples was higher for longer milled samples.

Fig. 4 shows magnetization as a function of magnetic field at 275 K and 350 K for S1 and S2 samples. Isotherms at 275 K for both samples show ferromagnetism while isotherms at 350 K show paramagnetic behavior for S2 and nearly paramagnetic behavior for S1

Fig. 5 shows hysteresis loops for samples S1 and S2. The inset shows low field details. Sample S2 has a higher coercivity of 30 Oe whilst S1 has 15 Oe. Increase in coercivity may have occurred due to the presence of pinning sites formed due to increased dislocation density and microcracks from longer milling in these materials which consistent with our previous observation in bulk materials [15].

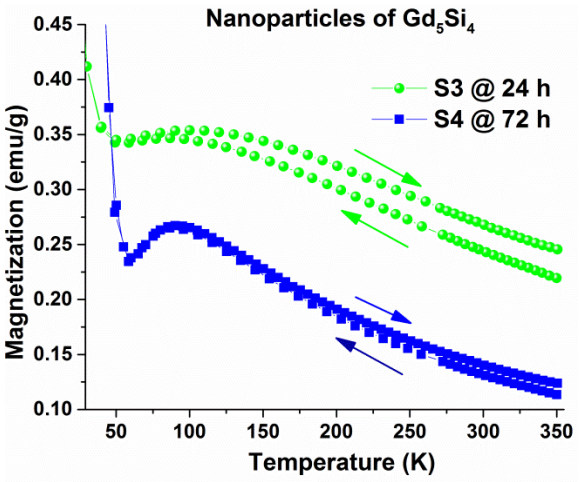

FIG. 6 Magnetization vs. Temperature at an applied field of 100 Oe for samples S3and S4 (longer milled samples)

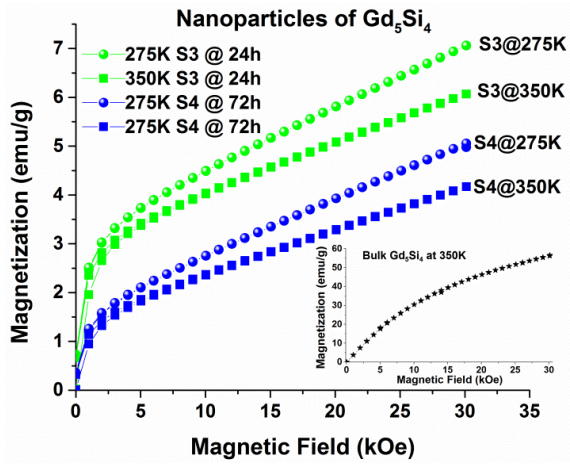

FIG. 7 M vs. H at 275 K and 350 K for samples S3 and S4. Both isotherms show ferromagnetism due to the presence of iron from ball milling media. Inset figure shows 350K isotherm for bulk sample.

Magnetization as a function of temperature at an applied field of 100 Oe is shown in Fig. 6 for S3 and S4. Bulk Gd_5Si_4 (Fig. 3) orders ferromagnetically at ≈340 K but the transition has disappeared in both ball-milled samples. M(T) behavior is complex reflecting several changes in the magnetic state at low temperatures, which warrant further investigations. The presence of a minor Gd_5Si_3 impurity is detected as a cusp observed near 80K in a bulk sample.

Magnetization as a function of magnetic field was also measured at two temperatures, 275 K and 350 K as shown in Fig. 7. Both isotherms show ferromagnetic-like behavior which persists to 350 K, confirming the presence of iron. The

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inset figure in Fig. 6 shows M-H behavior at 350K for bulk samples which shows nearly paramagnetic behavior for comparison with S3 and S4 samples. S3 and S4 display the lowest magnetization in spite of the fact that they have a high Fe percentage because, below 340K (Tc of Gd_5Si_4), S1 and S2 will have higher ferromagnetic Gd_5Si_4 content and Gd compounds have one of the highest Bohr magneton. However, above 340K, Gd5Si4 will be paramagnetic and samples S1 and S2 are expected to show lower magnetization compared to samples S3 and S4 but it is otherwise. This is because the magnetization is reducing with the milling time of the particles. Although S3 and S4 show ferromagnetic behavior at 275 and 350K but they are milled for much longer period which has reduced their magnetization significantly and hence show they have the lowest magnetization.

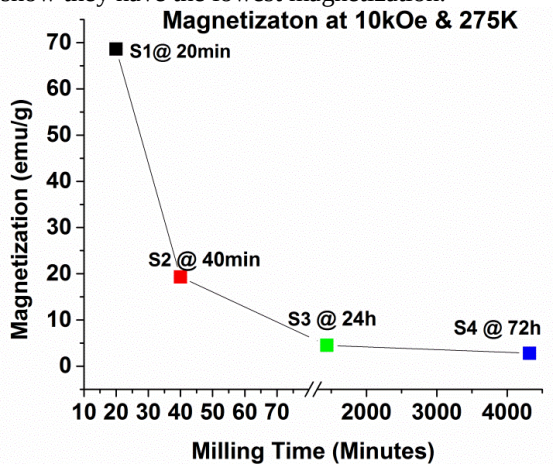

FIG. 8 Magnetization vs. milling time at 275 K and 10kOe for all the samples; S1 through S4 show that magnetization decreases significantly with increase in milling time which can also be observed from Fig 4 and Fig. 7.

Magnetization data from Fig. 4 and Fig. 7 were plotted vs. milling time at 275 K and 10kOe applied field as shown in Fig. 8. It can be clearly observed that the magnetization decreases significantly with increase in the milling time.

Overall, ball milling has a significant effect on the magnetism of Gd_5Si_4. The most obvious result is that prolonged milling leads to the disappearance of long-range ferromagnetic ordering at ~340K. The nature of low temperature magnetic states remains to be established.

IV. Conclusion

Nanoparticles of Gd_5Si_4 have been prepared by high energy ball milling with different milling times and milling intensities. Milling beyond 20 min leads to loss of crystallinity and the ferromagnetic transition observed in bulk Gd_5Si_4 at 340 K is also suppressed. Magnetic behaviors of nanoparticles milled longer than 20 min becomes complex and need further investigation.

Acknowledgment

Work at Ames Laboratory (preparation of bulk samples and nanoparticles, analysis of results and preparation of manuscript) was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Science and Engineering. Ames Laboratory is operated for DoE by Iowa State University under Contract No. DE-AC02-07CH11358. Barbara and James Palmer Endowment at the Department of Electrical and Computer Engineering of Iowa State University supported SEM, EDS, XRD, and magnetic measurements, analysis of results and manuscript preparation. Authors would also like to thank K. W. Denis and W. R. McCallum for helping with the SQUID measurements.

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