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Investigating phase transition temperatures of size separated gadolinium silicide magnetic nanoparticles

Abstract
Gadolinium silicide (Gd$_5$Si$_4$) nanoparticles (NPs) exhibit different properties compared to their parent bulk materials due to finite size, shape, and surface effects. NPs were prepared by high energy ball-milling of the as-cast Gd$_5$Si$_4$ ingot and size separated into eight fractions using time sensitive sedimentation in an applied dc magnetic field with average particle sizes ranging from 700 nm to 82 nm. The largest Gd$_5$Si$_4$ NPs order ferromagnetically at 316 K. A second anomaly observed at 110 K can be ascribed to a Gd$_5$Si$_3$ impurity. As the particle sizes decrease, the volume fraction of Gd$_5$Si$_3$ phase increases at the expense of the Gd$_5$Si$_4$ phase, and the ferromagnetic transition temperature of Gd$_5$Si$_4$ is reduced from 316 K to 310 K, while the ordering of the minor phase is independent of the particle size, remaining at 110 K.

Keywords
Nanoparticles, Paramagnetic materials, Materials processing, Silicon, Chemical analysis, Phase transitions, Nanomagnetism, X-ray diffraction, Ferromagnetic materials

Disciplines
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Investigating phase transition temperatures of size separated gadolinium silicide magnetic nanoparticles

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Gadolinium silicide (Gd$_5$Si$_4$) nanoparticles (NPs) exhibit different properties compared to their parent bulk materials due to finite size, shape, and surface effects. NPs were prepared by high energy ball-milling of the as-cast Gd$_5$Si$_4$ ingot and size separated into eight fractions using time sensitive sedimentation in an applied dc magnetic field with average particle sizes ranging from 700 nm to 82 nm. The largest Gd$_5$Si$_4$ NPs order ferromagnetically at 316 K. A second anomaly observed at 110 K can be ascribed to a Gd$_5$Si$_3$ impurity. As the particle sizes decrease, the volume fraction of Gd$_5$Si$_3$ phase increases at the expense of the Gd$_5$Si$_4$ phase, and the ferromagnetic transition temperature of Gd$_5$Si$_4$ is reduced from 316 K to 310 K, while the ordering of the minor phase is independent of the particle size, remaining at 110 K. © 2018 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.5007686

INTRODUCTION

Elemental gadolinium (electronic configuration: [Xe] 4f$^7$ 5d$^1$ 6s$^2$) has the largest spin-only magnetic moment among all other atoms in the periodic table. Its trivalent ion Gd$^{3+}$ with seven unpaired 4f electrons has long proton spin-lattice relaxation time (T1 $\approx$ 10$^9$ sec) at field strengths routinely used in medical Magnetic Resonance Imaging (MRI). This unique feature of gadolinium resulted in chelated gadolinium complexes being the most widely used T1 contrast agents (CA) in MRI. However, these compounds are paramagnetic at human body temperature making them suitable for use only as T1 CA. An alternative class of CA referred to as T2 is based on spin-spin relaxation process. Currently, superparamagnetic iron oxide nanoparticles (SPIONs) are beginning to be used as T2 CA. However, for continued improvement of biomedical imaging, there is an increasing need for improved CAs. Ferromagnetic gadolinium silicide (Gd$_5$Si$_4$) nanoparticles are shown to be useful as potential T2 CA for MRI with significantly reduced echo time (TE) compared to SPIONs. The production of the Gd$_5$Si$_4$ NPs via chemical synthesis routes has been challenging due to high oxygen affinity of gadolinium leading to significantly reduced magnetization. Therefore, top-down approach in an inert atmosphere is adopted not only to mitigate the oxidation of gadolinium but also increase yield through high scalability.

Furthermore, advances in nanotechnology are leading to the development of nanoscale materials with specifically engineered properties that differ from their bulk counterparts. NPs pharmacokinetics in vivo are largely influenced by their physicochemical properties such as morphology, size and other surface properties. The physicochemical properties in turn influence the magnetic behavior

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of individual NPs, since the magnetic properties of the NPs emerge from finite size and surface effects.\textsuperscript{10}

High imaging performance of CAs in MRI depends on their increased relaxivity coefficients ($r_1$ and $r_2$). In our recent publication we have shown that image contrast in MRI can be enhanced by higher saturation magnetization ($M_s$) of Gd$_5$Si$_4$ nanoparticles.\textsuperscript{2} In this study, the size dependent magnetic properties of Gd$_5$Si$_4$ NPs are investigated.

FIG. 1. SEM images of fractions. The figures inset shows average particle size distribution for each fraction.
METHODS

Gadolinium silicide (Gd$_5$Si$_4$) was synthesized by arc-melting of the stoichiometric mixture of gadolinium and silicon under Ar atmosphere. Gd$_5$Si$_4$ NPs were then prepared by high energy ball milling of the crushed ingot. The synthesis process is described in detail elsewhere.\textsuperscript{5,6,12} In order to separate NPs, one gram of the ball milled powder was added to 26 ml of ethyl alcohol. The suspension was sonicated for 4 hours to achieve thorough dispersion. Size separation was carried out by time sedimentation under applied dc magnetic field using NdFeB grade N52 permanent magnets placed below the beaker. Eight fractions ($S_1$, $S_2$, $S_3$, $S_4$, $S_5$, $S_6$, $S_7$ and $S_8$) separation of 3.25 ml each of the suspension were extracted from the bottom after 3, 10, 45, 180, 600, 1440, and 4320 minutes of sedimentation, with the last fraction $S_8$ being supernatant residue after the seventh extraction. After each extraction, the left over solution was sonicated for 30 minutes between $S_1$ and $S_3$ and 15 hours sonication for the rest in order to maintain good dispersion. The separated solutions were then evaporated at room temperature to obtain the powders.

Magnetic properties were measured in vibrating sample magnetometer (VSM, Quantum Design Versalab) in a constant magnetic field of 100 Oe between 50 K and 350K and hysteresis was measured in magnetic fields ranging -3T and 3T at 300 K.

RESULTS AND DISCUSSION

The morphology of the nanoparticles was characterized by Scanning Electron Microscopy (SEM, Hitachi Su-70) and quantitative elemental analysis of the nanoparticles was performed using spatially resolved energy dispersive X-ray spectroscopy (EDX). The images reveal irregularly shaped NPs with certain size distribution within each fraction. The advantage of such irregular shaped NPs over spherical shaped ones are that they are found to have better pharmacokinetics and possibly greater cell binding affinity.\textsuperscript{9} Diameters of the particles were individually measured using image analysis software (ImageJ) from the SEM digital images in order to determine the average particle size distribution. The resulting histogram is embedded with the SEM images of fractions. The SEM images show noticeable size variation along the fractions as shown in Fig. 1. EDX analysis confirms that there is no iron contamination in Gd$_5$Si$_4$ ingot from the production process (Fig. 2). X-ray diffraction (XRD) analysis (PANalytical X’Pert PRO) measurements reveal (Fig. 3) the presence of major phase Gd$_5$Si$_4$ and minor phase Gd$_5$Si$_3$. The obtained patterns for Gd$_5$Si$_4$ and Gd$_5$Si$_3$ are in good match with the reference peaks of the respective phases. The primary reference files for Gd$_5$Si$_4$ and Gd$_5$Si$_3$ matching reference peaks is sourced from "\textit{Calculated from ICSD using POWD-12++, (2004)}" which are based on reported structure Refs. 15 and 16. The phase content in $S_7$ and $S_8$

![FIG. 2. Elemental analysis of a fraction ($S_3$) in EDX.](image-url)
FIG. 3. (a) XRD patterns obtained from fractions. Reference peaks of Gd$_5$Si$_4$ and Gd$_5$Si$_3$ (bottom) matches with the patterns. (b) Average particle sizes decrease across fractions. Fractions are largely amorphous. The deficit of Si in the particle has come from the bulk material. The bulk material was prepared by arc-melting which was reported in the reference number. The deficit in Si in the bulk material could have been a result of incongruent melting of Gd and Si elements in the arc-melter, difference in vapor pressures of the Gd and Si, splintering of individual particles.

FIG. 4. (a) M-T curve for all fractions and pre-filtered sample (b) Curie temperatures ($T_c$) for each fraction (S1-S6) Gd$_5$Si$_4$ powder. (c) M-H curve for all fractions and pre-filtered sample; the figure inset showing coercivity ($H_c$) with respect to fractions.
elements in the arc-melting process due to uneven heat transfer and low thermal conductivity of Gd and Si.

The VSM measurements show changing Curie temperature for Gd$_5$Si$_4$ phase from 316 K for S1, S2 to 312 K for S3, S4 to 310 K for S5, S6 (Fig. 4(b)). Fractions S7 and S8 shows no presence of Gd$_5$Si$_4$ phase which corroborates with XRD analysis.

The Curie temperatures of all the phases present in the fractions are determined by the intersection point of the steepest tangent ($dM/dT$) to the M-T curve with the T axis. Curie temperature is observed at 110 K in all separation stages indicating presence of Gd$_5$Si$_3$ phase with the volume fraction of this phase increasing in subsequent fractions at the expense of Gd$_5$Si$_4$ phase. This is inferred from a qualitative observation made by comparison of the approximate analysis of heights of the M-T curve at the Curie temperatures of the respective phases. The increase in Curie temperature of Gd$_5$Si$_3$ from 70 K at its bulk form to 110 K in powdered form also reported by Hadimani et al.\textsuperscript{4} needs further exploration in order to fundamentally understand the cause for the significant shift in its Curie temperature. Another Curie temperature is observed at 290 K for all fractions indicating the presence of minuscule amount of elemental gadolinium. Presence of elemental gadolinium in the samples may be counter-intuitive as it oxidizes in oxygen rich environments however, the gadolinium oxide forms a barrier shell on the surface preventing further oxidation. Hence, gadolinium can be detected in our M-T measurements. The M-H curves at 300 K exhibits ferromagnetic behavior descending to paramagnetic as we move from S1 to S8 fraction. Coercivity (Hc) obtained from hysteresis plots show (inset of Fig. 4(c)) that it increases with decrease in particle size across fractions. This agrees with reports in the literature, where the coercivity increases with decrease in particle size until it reaches single domain and then decreases toward zero where it becomes superparamagnetic.\textsuperscript{7,10,17}

CONCLUSION

The study reveals phase and size separation of Gd$_5$Si$_4$ nanoparticles could be successfully carried out with the time sensitive sedimentation technique under applied dc magnetic field using a N52 NdFeB permanent magnet. Average nanoparticle sizes decreased as the sedimentation time increased across fractions. Applying dc magnetic field in the separation process resulted in separation of phases (ferromagnetic Gd$_5$Si$_4$ phase from paramagnetic Gd$_5$Si$_3$ phase and other impurities). Curie temperature of major phase Gd$_5$Si$_3$ decreased from 316 K to 310 K across fractions indicating decrease in average Gd$_5$Si$_4$ particle sizes while the Curie temperature remained constant at 110 K and 290 K for Gd$_5$Si$_3$ phase and elemental gadolinium phase respectively being unaffected by particle size variation.

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