IRis

Northeastern University

Electrical and Computer Engineering Faculty Publications

Department of Electrical and Computer Engineering

May 01, 2010

# Structural and size dependent magnetic properties of single phase nanostructured gadolinium-iron-garnet under high magnetic field of 32 tesla

C. N. Chinnasamy

J. M. Greneche

M. Guillot

B. Latha

T. Sakai

***See next page for additional authors***

## Recommended Citation

Chinnasamy, C. N.; Greneche, J. M.; Guillot, M.; Latha, B.; Sakai, T.; Vittoria, C.; and Harris, V. G., "Structural and size dependent magnetic properties of single phase nanostructured gadolinium-iron-garnet under high magnetic field of 32 tesla" (2010). *Electrical and Computer Engineering Faculty Publications.* Paper 126. http://hdl.handle.net/2047/d20002297

This work is available open access, hosted by Northeastern University.

**Author(s)**
C. N. Chinnasamy, J. M. Greneche, M. Guillot, B. Latha, T. Sakai, C. Vittoria, and V. G. Harris

This article is available at IRis: http://iris.lib.neu.edu/elec_comp_fac_pubs/126

AIP Journal of Applied Physics

# Structural and size dependent magnetic properties of single phase nanostructured gadolinium-iron-garnet under high magnetic field of 32 tesla

C. N. Chinnasamy, J. M. Greneche, M. Guillot, B. Latha, T. Sakai et al.

Citation: J. Appl. Phys. **107**, 09A512 (2010); doi: 10.1063/1.3357326
View online: http://dx.doi.org/10.1063/1.3357326
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v107/i9
Published by the American Institute of Physics.

## Related Articles

Relaxor ferroelectric behavior of BaMnO3 (2H) at room temperature
Appl. Phys. Lett. 100, 042904 (2012)

The effect of Li-substitution on the M-phases of AgNbO3
J. Appl. Phys. 111, 024107 (2012)

A comparative density functional study of the low pressure phases of solid ZnX, CdX, and HgX: Trends and relativistic effects
J. Chem. Phys. 136, 034504 (2012)

(PbS)32: A baby crystal
J. Chem. Phys. 136, 024317 (2012)

Relaxor ferroelectric characteristics of Ba5LaTi3Nb7O30 tungsten bronze ceramics
Appl. Phys. Lett. 100, 012902 (2012)

## Additional information on J. Appl. Phys.

Journal Homepage: http://jap.aip.org/
Journal Information: http://jap.aip.org/about/about_the_journal
Top downloads: http://jap.aip.org/features/most_downloaded
Information for Authors: http://jap.aip.org/authors

ADVERTISEMENT

Downloaded 30 Jan 2012 to 129.10.105.52. Redistribution subject to AIP license or copyright; see http://jap.aip.org/about/rights_and_permissions

# Structural and size dependent magnetic properties of single phase nanostructured gadolinium-iron-garnet under high magnetic field of 32 tesla

C. N. Chinnasamy,[1] J. M. Greneche,[2] M. Guillot,[3,a)] B. Latha,[1] T. Sakai,[1] C. Vittoria,[1] and V. G. Harris[1]

[1]*Center for Microwave Magnetic Materials and Integrated Circuits, Northeastern University, Boston, Massachusetts 02115, USA*

[2]*Laboratoire de Physique de L'Etat Condensé, UMR CNRS 6087, Université du Maine, 72085 Le Mans Cedex 9, France*

[3]*Laboratoire National des Champs Magnétiques Intenses, CNRS BP 166, 38042 Grenoble, France*

(Presented 20 January 2010; received 16 November 2009; accepted 31 December 2009; published online 28 April 2010)

Here we report the single phase nanostructured $Gd_3Fe_5O_{12}$ garnets with different grain sizes (bulk, 75, 47, 35, and 22 nm) were prepared by ball milling for various milling times. Both the average grain size and the lattice parameter were estimated from the x-ray diffraction line broadening. The $^{57}$Fe Mössbauer spectra were recorded at 300 and 77 K for the samples with different grain sizes clearly evidenced the formation of $Fe^{2+}$ ions induced by milling and the content of $Fe^{2+}$ increases with milling time. At 4.2 K, a significant increase in saturation magnetization (+11%) has been observed for the 47 nm particles. The magnetization is strongly applied field dependent and no saturation effect is observed even at fields as high as of 320 kOe. The results presented here have been explained in terms of the key role played by the $Fe^{2+}$ ions. © *2010 American Institute of Physics*. [doi:10.1063/1.3357326]

## I. INTRODUCTION

Rare earth iron garnets (REIG) are promising candidates for use in high performance microwave and electrochemical devices owing to its high resistivity, high Curie temperature, and high chemical stability and possess unique magnetic, optical, thermophysical, and mechanical properties.[1–7] The general chemical formula for the REIG is $\{R_3^{3+}\}_c[Fe_2^{3+}]_a(Fe_3^{3+})_dO_{12h}^{2-}$. The unit cell of the garnet is composed of eight formula units forming a complex cubic lattice constituted by altogether 160 ions on specific lattice positions, i.e., 96 $O^{2-}$ ions on *h* sites and three groups of trivalent metal ions distributed on 24 *c* sites $\{R^{3+}\}$, 16 octahedral *a* sites $[Fe^{3+}]$ and 24 tetrahedral *d* sites $(Fe^{3+})$, respectively. Note that the Gd magnetic moment is insensitive to the crystalline field and to the superexchange anisotropy due to the absence of net orbital angular momentum (L=0).

The dominating superexchange interaction renders the $[a]$ and $(d)$ sites magnetic moments antiparallel and determines the Curie temperature ($T_C$) whereas the magnetization of $Gd^{3+}$ ion is opposite to the resultant magnetization of $Fe^{3+}$ ion sublattices giving rise to ferrimagnetism. This is possible only because the superexchange interaction among the $Fe^{3+}$ ions polarizes the paramagnetic rare earth ions magnetically.[8] At the compensation temperature ($T_{comp}$), $M\{Gd_3^{3+}\}$ at the *c*-sites is equal and opposite to the resultant of $Fe^{3+}$ ion sublattice of the $[a]$ and $(d)$ sites. The compensation ($T_{comp}$) and Curie temperature ($T_C$) of the bulk GdIG are 295 K and 566 K, respectively.[2]

In spinel ferrites, the grain size reduction induces the competition between the ferro- and antiferromagnetic exchange interactions arising from Fe clustering, the breaking of superexchange bonds, spin canting, and formation of $Fe^{2+}$ charge state due to oxygen vacancies produced while milling. As a result, the change in cation distribution, magnetization, coercivity, and enhanced Néel temperature has been proved.[9–13] However, there is no report in the literature, to the best of our knowledge, on the synthesis of *single phase* nanostructured GdIG with various grain sizes. In the past few attempts have been made to synthesize nanostructured GdIG using various techniques and when the size of the particles reduced to nanoscale it was found to decompose into rare earth orthoferrite, and other rare earth and iron oxide phases.[14–17] Here, single phase nanostructured $Gd_3Fe_5O_{12}$ garnets have been prepared using the ball milling technique and its structural and magnetic properties were studied in detail.

## II. EXPERIMENT

$Gd_3Fe_5O_{12}$ particles were synthesized in polycrystalline form by the solid-state reaction technique from a mixture of $\alpha$-$Fe_2O_3$ (Aldrich, 99.99%) and $Gd_2O_3$ (Aldrich, 99.99%) in nominal compositions of 5:3. The crystal structure was characterized by x-ray powder diffraction using Cu $K\alpha$ radiation ($\lambda$=1.5404 Å) in Rigaku Dimax 2000 diffractometer. Milling of the as-prepared particles was carried out for different durations in a controlled atmosphere using a planetary ball mill (Fritsch Pulverisette, P6) to reduce the grain size.

$^{57}$Fe Mössbauer spectrometry was carried out at 300 and 77 K using a constant acceleration Mössbauer spectrometer with a source of 25 mCi $^{57}$Co diffused into a Rh matrix. Natural iron foil was used as a standard for velocity calibration. The dc magnetization studies were carried out using a

a)Electronic mail: maurice.guillot@grenoble.cnrs.fr.

 © 2010 American Institute of Physics

Downloaded 30 Jan 2012 to 129.10.105.52. Redistribution subject to AIP license or copyright; see http://jap.aip.org/about/rights_and_permissions

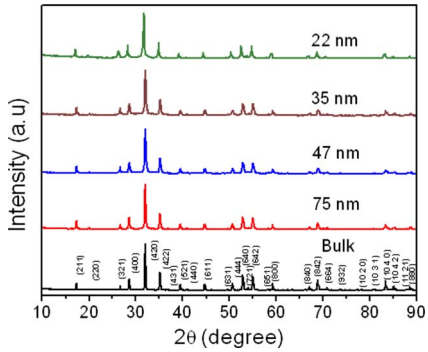


FIG. 1. (Color online) X-ray diffraction pattern of bulk and nanostructured $Gd_3Fe_5O_{12}$.

homemade magnetometer under a high continuous magnetic field of up to 320 kOe using the extraction technique in the range of 4–300 K at the Grenoble High Magnetic Field Laboratory, Grenoble, France. The $T_C$ of the $Gd_3Fe_5O_{12}$ nanoparticles were measured by using the Lakeshore 2500 vibrating sample magnetometer in a high temperature set up.

## III. RESULTS AND DISCUSSION

The x-ray diffractograms of the bulk and milled $Gd_3Fe_5O_{12}$ garnet particles are compared in Fig. 1. The milled $Gd_3Fe_5O_{12}$ garnet particles retain their single phase structure (JCPDS-48–0077). The average grain size was determined by using the Scherrer formula from the full width at half maximum of the (422) diffraction peak for different milling times. The initial increase in the lattice parameter is due to the expansion of the lattice as a result of the cation redistribution and mechanically induced stresses. The subsequent decrease in the lattice parameter after 10 h milling is attributable to the possible mechanically induced changes in the bond lengths and angles.[9]

The $^{57}$Fe Mössbauer spectra were recorded at 300 and 77 K for the nanostructured $Gd_3Fe_5O_{12}$ having different grain sizes are illustrated in Fig. 2. The spectra were least square fitted and the refined values of the hyperfine parameters were then determined. For the as-prepared $Gd_3Fe_5O_{12}$, the spectra were described by means of three sextets corresponding to three different $Fe^{3+}$ environments (octahedral sites [$12a_1$ and $4a_1$] and tetrahedral ($24d$) sites, respectively). There is no evidence for the presence of $Fe^{2+}$ charge state in the as-prepared garnets. On increasing the milling time, one observes the progressive occurrence of a central quadrupolar feature at both 300 and 77 K, as is shown in Fig. 2, in addition to three magnetic sextets with decreasing intensity but increasing linewidth compared to that of the bulk. These later components are unambiguously attributed to crystalline GdIG phase with structurally disordered $Fe^{3+}$ environment induced during milling. The quadrupolar feature has to be decomposed at both temperatures into two broad line quadrupolar doublets. They are characterized by two different isomer shift values which allow the presence of ferric and ferrous species to be identified; it is important to emphasize that the intensity of the ferric doublet is systematically higher at 300 K while the $Fe^{2+}$ content linearly increases with the milling time from the hyperfine data estimated from the ab-

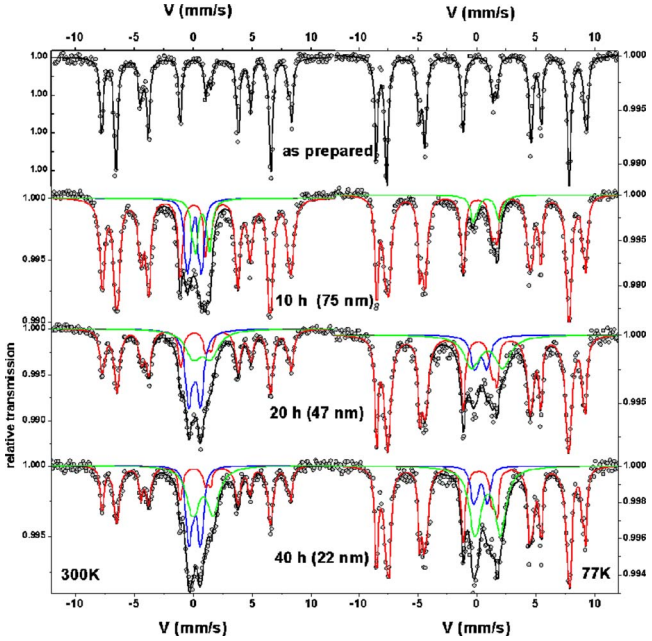


FIG. 2. (Color online) Mössbauer spectra recorded at 300 and 77 K for the as-prepared, 10, 20, and 40 h milled $Gd_3Fe_5O_{12}$.

sorption areas at 300 and at 77 K (Fig. 3). The reduction in some of the $Fe^{3+}$ ions to $Fe^{2+}$ ions giving rise to the formation of oxygen vacancies as previously reported in milled $ZnFe_2O_4$ sample.[13] In all the nanocrystalline samples, the tetrahedral component was well described with at least two well defined sextets suggesting some local distortions. However, we did not observe any spin canting.

Due to the inability to saturate the magnetization, magnetization measurements were performed on all the samples in the temperature range of 4.2–300 K under continuous magnetic fields up to 320 kOe and the first quadrant hysteresis loops are shown in Fig. 4. We will discuss here the 4.2 K results only. It is noted that the 30 h (35 nm) milled sample show lower magnetization values than the other studied ones.

The measured magnetization (M) for the as-prepared GdIG is found equal to 15.9 $\mu_B$ mol$^{-1}$ at 4.2 K and this value confirms that all the Fe and Gd ions are in a trivalent state according to a pure ferrimagnetic ordering of GdIG single crystal. It is also worth noting that the saturation field ($M_{sat}$) starts even at an applied field of 5 kOe for the as-

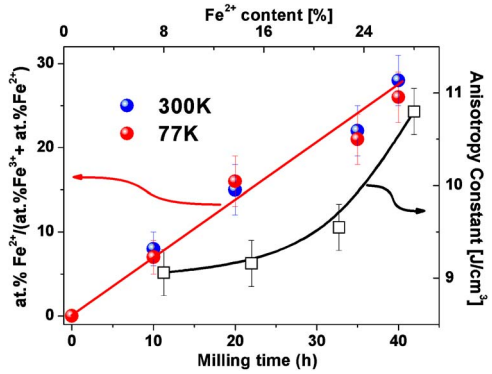


FIG. 3. (Color online) $Fe^{2+}$ content vs the milling time and calculated anisotropy constant.

Downloaded 30 Jan 2012 to 129.10.105.52. Redistribution subject to AIP license or copyright; see http://jap.aip.org/about/rights_and_permissions

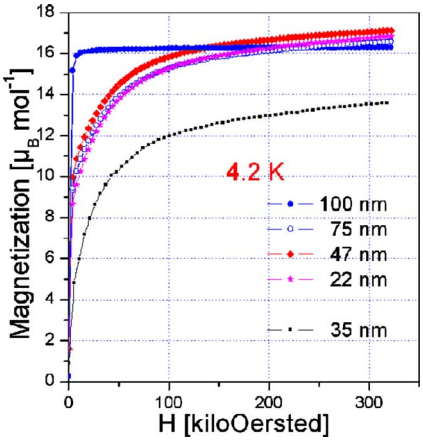


FIG. 4. (Color online) Isothermal magnetization curves at 4.2 K.

prepared GdIG. When the grain size is reduced below 100 nm, the M is strongly applied field dependent and no saturation is observed even under the highest applied field of 320 kOe. The $M_{sat}$ attains the bulk value of 16 $\mu_B$ mol$^{-1}$ only when the external applied field (H) is equal to 130, 200, and 240 kOe for the 20 h (47 nm), 40 h (22 nm), and 10 h (75 nm) milled samples, respectively at 4.2 K.

In the 170–320 kOe field range the magnetization curves of the different milled samples are very well (within $\pm 1\%$) described by the law of approach to saturation $M = M_{sat}(1 - b/H^2)$. According to Néel[18] the b coefficient is determined by the magnetocrystalline anisotropy and given by $b = 8\ K^2/105\ (M_{sat})^2$. At 4.2 K, $M_{sat}$ was found equal to 16.8 $\mu_B$ mol$^{-1}$ for the 10 h, 17.4 $\mu_B$ mol$^{-1}$ for the 20 h, and 17.1 $\mu_B$ mol$^{-1}$ for the 40 h samples, respectively; for the 35 h milled sample $M_{sat}$ is only equal to 14 $\mu_B$ mol$^{-1}$ and remains much smaller than the bulk value. The so-calculated variation in K is reported in Fig. 3 versus the $Fe^{2+}$ content where a large increase in K is observed when the milling time increases.

The modified formulae of our GdIG particle is given by $\{Gd_3^{3+}\}\ (Fe_{3(1-r)}^{3+}Fe_{3r}^{2+})\ [Fe_{2(1-s)}^{3+}Fe_{2s}^{2+}]\ O_{12-2.5p}^{2-}$ taking into account the presence of oxygen vacancies related to the $Fe^{2+}$ content (p). Assuming that only the $Fe^{3+}$ ions contribute to the ferrite magnetization r and s values were calculated using the p and $M_{sat}$ values deduced from the Mössbauer spectra and high field behavior analysis, respectively. The detailed analysis on the effect of $Fe^{2+}$ ion in the octahedral and tetrahedral site in garnets will be explained elsewhere.[19] A study of the distribution of $Fe^{3+}$ over the two magnetic sites explains then why $M_{sat}$ varies around the bulk value although the reduction from $Fe^{3+}$ to $Fe^{2+}$ increases rapidly with the increasing of milling time that corresponds to a decrease in the grain size. The particular behavior of the 35 h milled samples is then explained by the fact that the octahedral site contains the largest part of $Fe^{2+}$ ion since s and r are found to be equal to 0.28 and 0.15, respectively. On the contrary for the 40 h milled sample, s=0.19 and r=0.29; that means for this sample 71% (81%) of the Fe ions are in a trivalent state in the tetrahedral (octahedral) sublattice.

Also, we would like to note that the compensation temperature ($T_{comp}$) values of the nanostructured garnets are few degrees higher than that of the bulk. However, the Curie temperature ($T_C$) of the various sized nanostructured GdIG samples are found to be significantly higher than that of the bulk ($T_C$ varies from 591 K for the bulk to 628 K in the sample milled for 20 h with 47 nm mean grain size).

## IV. CONCLUSIONS

Single phase nanostructured GdIG particles with different grain sizes were prepared using the ball milling technique. The average grain size decreases with milling time and the lattice parameter initially increases due to the expansion of the lattice as a result of the cation redistribution and mechanically induced stresses and decreases for higher durations of milling. Mössbauer spectroscopy studies shows that there is no evidence for the presence of $Fe^{2+}$ charge state in the as-prepared garnets. However, milling induces the oxygen vacancies and hence the presence of $Fe^{2+}$ content increases rapidly with the increasing of milling time that corresponds to a decrease in the grain size. When the grain size is reduced below 100 nm, the magnetization is strongly applied field dependent and no saturation is observed even under the highest applied field of 320 kOe. The magnetic moment values of the nanostructured garnets are approximately 11% higher than that of the bulk value at 4.2 K except for the 35 h milled sample and it depends on the population of $Fe^{2+}$ ion distribution in tetrahedral and octahedral sites. A large increase in magnetocrystalline anisotropy is also observed in the nanostructured GdIG garnet particles.

[1] L. Néel, Ann. Phys. (Paris) **3**, 137 (1948).
[2] R. Pauthenet, J. Appl. Phys. **29**, 253 (1958).
[3] G. F. Dionne, J. Appl. Phys. **47**, 4220 (1976).
[4] G. Winkler, *Magnetic Garnets* (Friedr. Vieweg & Sohn, Braunschweig, 1981), Chap. 2.
[5] A. H. Eschenfelder, *Magnetic Bubble Technology* (Springer, New York, 1981).
[6] T. Yamagishi, J. Awaka, Y. Kawashima, M. Uemura, S. Ebisu, S. Chikazawa, and S. Nagata, Philos. Mag. **85**, 1819 (2005).
[7] M. Uemura, T. Yamagishi, S. Ebisu, S. Chikazawa, and S. Nagata, Philos. Mag. **88**, 209 (2008).
[8] M. A. Gilleo, *Physics of Magnetic Garnets* (North-Holland, Amsterdam, 1978), p. 15.
[9] C. N. Chinnasamy, A. Narayanasamy, N. Ponpandian, K. Chattopadhyay, H. Guérault, and J. M. Greneche, J. Phys.: Condens. Matter **12**, 7795 (2000).
[10] N. Ponpandian, A. Narayanasamy, C. N. Chinnasamy, N. Sivakumar, J. M. Greneche, K. Chattopadhyay, K. Shinoda, B. Jeyadevan, and K. Tohji, Appl. Phys. Lett. **86**, 192510 (2005).
[11] C. N. Chinnasamy, A. Narayanasamy, N. Ponpandian, K. Chattopadhyay, K. Shinoda, B. Jeyadevan, K. Tohji, K. Makatsuka, T. Furubyashi, and I. Nakatani, Phys. Rev. B **63**, 184108 (2001).
[12] V. Šepelák, A. Feldhoff, P. Heitjans, F. Krumeich, D. Menzel, F. J. Litterst, I. Bergmann, and K. D. Becker, Chem. Mater. **18**, 3057 (2006).
[13] G. F. Goya and H. R. Rechenberg, J. Magn. Magn. Mater. **196–197**, 191 (1999).
[14] S. Geller, J. Appl. Phys. **31**, S30 (1960).
[15] A. Paesano, S. C. Zanata, S. N. De Mediros, L. F. Cotica, and J. B. M. Da Cunha, Hyperfine Interact. **161**, 211 (2005).
[16] R. J. Joseyphus, A. Narayanasamy, A. K. Nigam, and R. Krishnan, J. Magn. Magn. Mater. **296**, 57 (2006).
[17] S. C. Zanatta, L. F. Cotica, A. Paesano, S. N. de Medeiros, J. B. M. da Cunha, and B. Hallouche, J. Am. Ceram. Soc. **88**, 3316 (2005).
[18] L. Néel, J. Phys. Radium **9**, 184 (1948).
[19] H. Pascard, Phys. Rev. B **30**, 2299 (1984).

Downloaded 30 Jan 2012 to 129.10.105.52. Redistribution subject to AIP license or copyright; see http://jap.aip.org/about/rights_and_permissions