

DETAILED CRYSTALLIZATION STUDY OF CO-PRECIPIATED $Y_{1.47}Gd_{1.53}Fe_5O_{12}$ AND RELEVANT MAGNETIC PROPERTIES

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The crystallization process of co-precipitated $Y_{1.5}Gd_{1.5}Fe_5O_{12}$ powder heated up to 1000 °C at rate of 5 °C min⁻¹ was investigated. Above 810 °C crystalline $Y_{1.47}Gd_{1.53}Fe_5O_{12}$ was obtained with a lattice parameter of 12.41 Å and a theoretical density of 5.84 g cm⁻³. Dry pressed rings were sintered at 1270 and 1320 °C, increasing the grain-size from 3.1 to 6.5 μm, the theoretical density by 87.6 to 95.3% and decreasing H_c from 2.9725 to 1.4005 Oe. Additionally, H_c increased when the frequency of the hysteresis graph varied from 60 Hz to 10 kHz, the curie temperature was 282.4 °C and M_s equalled 9.25 emu g⁻¹ (0.17 kG) agreeing well with the B_s -value of the hysteresis graph and literature values.

Keywords: $Y_{1.5}Gd_{1.5}Fe_5O_{12}$; crystallization; magnetic properties.

INTRODUCTION

Both Yttrium Iron Garnet (YIG) and Gadolinium Iron Garnet (GdIG) continue to be studied due to diversified scientific and technological motivations, such as: magnetism^{1,2}, thin films^{3,4}, environmental stability^{5,6}, structural defects and faults⁷, synthesis⁸, nanocrystals and nanocomposites⁹, magneto-optical properties and applications¹⁰⁻¹², as well as wireless infrastructures¹³. Despite of this advanced status of science and technology on YIG and GdIG, there is still considerable lack of scientific knowledge on: crystallization of GdYIG from mixed gadolinium-yttrium hydroxides generated by means co-precipitation method of synthesis; and effects of sintering temperature on microstructure and magnetic properties of GdYIG. These points are evidenced in the concise literature review that follows below.

Synthesis by powder mixing method

Ristic *et al.*⁸ prepared YIG samples by powder mixing method using ball-milled reagent-grade mixture of Y_2O_3 and Fe_2O_3 in a 3:5 ratio. The fractions of Y_2O_3 , $\alpha-Fe_2O_3$, $YFeO_3$ and YIG presented in the product depended on the calcination's temperature. Heating at 1200 °C (for 2 h) conducted to the formation of YIG and small amounts of $YFeO_3$, while heating at 1300 °C (for 1 h) produced YIG containing smaller amount of $YFeO_3$. Others calcination's temperatures and times were 900 °C (for 1 h) and 1000°C (for 2 h). In both cases the results were worse than in the 1200 °C case.

Laval¹⁴ synthesized GdYIG by powder mixing method and calcinations in oxygen at 1235 °C. It was then remilled (particle size $\leq 1 \mu m$), cold-pressed (700 N/cm²) into small cylinders (7 mm in diameter by 10 mm high, about 2 g in weight) and sintered them at 1460 to 1480 °C, obtaining sinters with 94% of theoretical density and mean grain size of 5 to 6 μm. The results showed that Gd³⁺ produces pre-transformed nuclei in the YIG matrix and promotes the exsolution of magnetite in the YIG's matrix.

Beregi *et al.*¹⁵ investigated the synthesis of YIG by powder mixing method and found out that formation of $YFeO_3$ together with YIG had already begun at 700 °C (traces of garnet and orthoferrite phases were detected at 800 °C). The amount of $YFeO_3$ reached its maximum at 1100 °C. Just above this temperature a sharp increase of the YIG phase took place. Traces of Fe_3O_4 were found in samples sintered at 1000 and 1100 °C.

Summarizing, it is difficult to produce a fine-grained homogeneous and single phase $Y_{1.5}Gd_{1.5}Fe_5O_{12}$ garnet powder by powder mixing method.

Synthesis by co-precipitation method

Ristic *et al.*⁸ synthesized YIG samples by co-precipitation using a Y_2O_3/Fe_2O_3 3/5 ratio. The calcination of the co-precipitated hydroxide at 900 °C showed the formation of YIG as a dominant phase, and $YFeO_3$ and Y_2O_3 as associated phases; whereas calcinations at 1200 °C conducted to the formation of YIG and a small amount of $YFeO_3$. The starting hydroxides were co-precipitated from an aqueous solution (pH = 10.4) of nitrates of yttrium and iron. The dried hydroxides were heated up to 600 °C, cooled down and pressed into tablets, which were then heated up to 900 °C (for 2, 6 or 8 h) or 1200 °C (for 2 h).

Music *et al.*¹⁶ synthesized $(1-x)Fe_2O_3 \cdot xGd_2O_3$ ($0 \leq x \leq 1$) by co-precipitation from aqueous solutions of iron and gadolinium nitrates, by adding ammonium hydroxide, and step-wise drying and heating of mixed hydroxide up to each of the following temperatures: 200, 300, 500, 600 °C, where it was kept for 1h, and heated up to 900 °C where again it was kept for 4 h. While $Fe(OH)_3$ converted to Fe_2O_3 at 200 °C (for 1 h), $Gd(OH)_3$ only converted entirely to Gd_2O_3 at 900 °C (for 1 h), where the co-precipitate became entirely crystalline. Its phase constitution depended on the Gd content of the mixture, consisting of a mixture of $Gd_3Fe_5O_{12}$, $GdFeO_3$, Fe_2O_3 and Gd_2O_3 , while $GdFeO_3$ content decreased for Gd content above $x = 0.50$.

Godoi *et al.*¹⁷ co-precipitated yttrium and iron hydroxides from an aqueous solution of yttrium and iron chlorides, plus

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polyvinylpyrrolidone (PVP), pre-heated up to 90 °C, by using urea and/or ammonium hydroxide as the precipitation agent, followed by ageing for 3 h at 90 °C, filtering and drying, and calcination at 1100 °C for 4 h to obtain cubic phase YIG. Crystallization of the mixed hydroxide/oxide started at 800 °C and resulted on orthorhombic phase up to 1000 °C, being converted to cubic phase above 1100 °C.

Cho *et al.*¹⁸ obtained successful hydrothermal synthesis of a cubic phase YIG at 200 °C for 6 h from mixed hydroxides co-precipitated at pH = 10.5 and 25 °C using ammonium hydroxide.

These literature data show that chemical co-precipitation method is a good way to produce fine-grained $Y_{1.5}Gd_{1.5}Fe_5O_{12}$ garnet powder, but also that there is not yet a precise definition of the minimum calcination temperature required for obtaining it as single phase. The motivation and original contribution of the present work are to provide a breakthrough answer to this question by means of detailed and well-documented x-ray diffraction patterns.

EXPERIMENTAL

The experimental procedure for co-precipitation of mixed hydroxides of Gd, Y and Fe from nitrate solutions was based on the results of a previous thermodynamics analysis¹⁹. Aimed at producing co-precipitate of mixed oxides containing Gd, Y and Fe in stoichiometric amount to the $Y_{1.5}Gd_{1.5}Fe_5O_{12}$, the due concentrations of Gd, Y and Fe nitrates were dissolved in distilled water under intensive stirring and hot bath at 90 °C. After cooling down to room temperature, this solution was supplied drop-wise into an intensively stirred KOH solution which concentration was enough to assure a final 10-12 pH range. The dark brown coprecipitate of $Y(OH)_3$, $Gd(OH)_3$ and $Fe(OH)_3$ was vacuum filtered, washed with distilled water several times until complete elimination of K^+ ions. The purified coprecipitated was dried inside a desiccator²⁰ for 24 h and then dried by heating in an oven at 60 °C for 1 h. Finely milled portions of the dried coprecipitate were used to carry out TGA and DTA (Shimadzu DTA-50 and TGA-50H). From those, it was extracted the necessary data to support the decision to perform batch calcination²¹ at 814 °C for 5 h and convert the coprecipitate into a crystalline dark green YGdIG precursor. This product was characterized by SEM²², using Zeiss DSM 940-A instrument at 20 to 25 kV; by XRD²², using a Rigaku DMXA 2200 apparatus and Cu $K\alpha$ ($\lambda = 1,542\text{\AA}$) and ICDD-PDF/2001 database; and by XRF²², using a Philips PW-2400 apparatus and Vibrating Sample Magnetometer.

Finely milled calcined powder (50 vol% of particles smaller than 4.47 μm , according to Malvern laser scattering) received addition of 2 wt% polyvinylalcohol (PVA) binder (as 15 wt% aqueous solution)^{23,24}. Then, it was dry pressed with 500 kg/cm^2 in a steel die in order to obtain rings with the following dimensions: 2 cm external diameter, 1 cm internal diameter and 0.4 cm height. The sintering process^{15,25} was carried in air at atmospheric pressure and in 1270 and 1320 °C temperatures. The heating schedule was designed with 3 ramps (one of them for cooling down) and 2 dwells. The first ramp arised to 480 °C at 2.7 °C/min rate, in order to allow the binder to volatilize. This binder elimination process²⁶ was completed during the 1 h interval in which it stayed at the 480 °C dwells. Next stage was a ramp up to the sintering temperature, using a heating rate of 8 °C/min. The total sintering time was 5 h for all the compacts. Cooling down was carried out in natural way, taking about 15 h.

Sintered samples were analyzed by hysteresisgrapher (where the sintered rings received a polymer coated copper winding [AW6-29]), vibrating sample magnetometer, SEM, EDS, and helium pycnometer²⁷.

RESULTS AND DISCUSSION

Figure 1 presents the differential thermal analysis (DTA) and the thermal-gravimetric curve (TGA) of the dried co-precipitate powder. DTA curve contains an endothermic peak below 100 °C and an exothermic one at about 810 °C. The TGA curve contains a great weight loss (87.34 wt%) from 25 °C until 500 °C due to the initial moisture loss and to the dehydration loss in the conversion of hydroxide to mixed amorphous oxides of Gd, Y and Fe. A continuously decreasing rate of weight loss (12.66 wt% of the total mass lost) takes place in the 500 to 1000 °C range, completing the thermal decomposition of mixed hydroxides, resulting in YGdIG. It may be concluded that exothermic peak at 810 °C, as seen in Figure 1a, corresponds to crystallization of the mixed anhydrous oxide of yttrium, gadolinium and iron, obtaining crystalline yttrium-gadolinium-iron garnet.

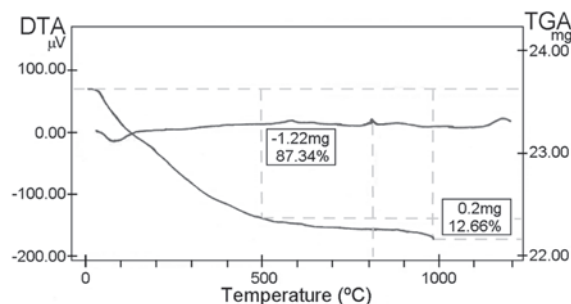


Figure 1. Thermal-gravimetric and differential thermal analysis curves of the dried co-precipitate

Figures 2 and 3 present XRD patterns of the co-precipitate after calcinations at several increasing temperatures in the 200–814 °C range, showing the evolution of the transformation from the amorphous co-precipitate (Figure 2a) to entirely crystalline material (Figure 3). The calcinations product is still amorphous up to 600 °C (Figure 2e). Quite well defined peaks appear when calcination is carried out (at 700 °C, Figure 2g). In Figure 3, XRD pattern of the sample calcined at 814 °C has all the peaks indexed. Therefore, 810 °C is indeed the answer to the question “what is the minimum calcination temperature required to get single phase crystalline $Y_{1.47}Gd_{1.53}Fe_5O_{12}$?”.

Figures 4a and 4b show the SEM micrograph of the YGdIG powder calcined at 814 and 1200 °C, respectively, displaying cubic grains, which diameter varies in the 0.5 nm- 1 μm range along the calcining temperature considered, while Figure 5a presents narrow hysteresis loop of the powder as calcined at 814 °C, as determined by Vibrating Sample Magnetometer, where it is seen a coercive force equal to 100 Oe, which is too high for a soft ferrite. Of course, the high porosity and the very small grain size, typical of ferrite powders calcined at low temperature, explain well this result.

Figures 4c and 4d show the SEM micrograph of the YGdIG ceramic rings sintered at 1270 and 1320 °C, respectively, where it is seen high densification and larger grain sizes. XRD patterns of the sintered rings determined the density and the lattice parameter values to be 5.84 g/cm^3 and 12.41 \AA , respectively. Figure 6 shows the XRD pattern of the $Y_{1.47}Gd_{1.53}Fe_5O_{12}$ sintered at 1320 °C, and displays the indexed diffractions lines of this YGdIG as resulting from lattice parameter distortion relative to the simple rare-earth iron garnets from which it originates ($Y_3Fe_5O_{12}$ and $Gd_3Fe_5O_{12}$).

Table 1 presents some results of the magnetic properties of the ceramic rings, sintered at 1270 and 1320 °C. They were determined by using Walker Scientific AMH-20 Hysteresisgrapher. Notice that increase in frequency produces increases of maximum induction,

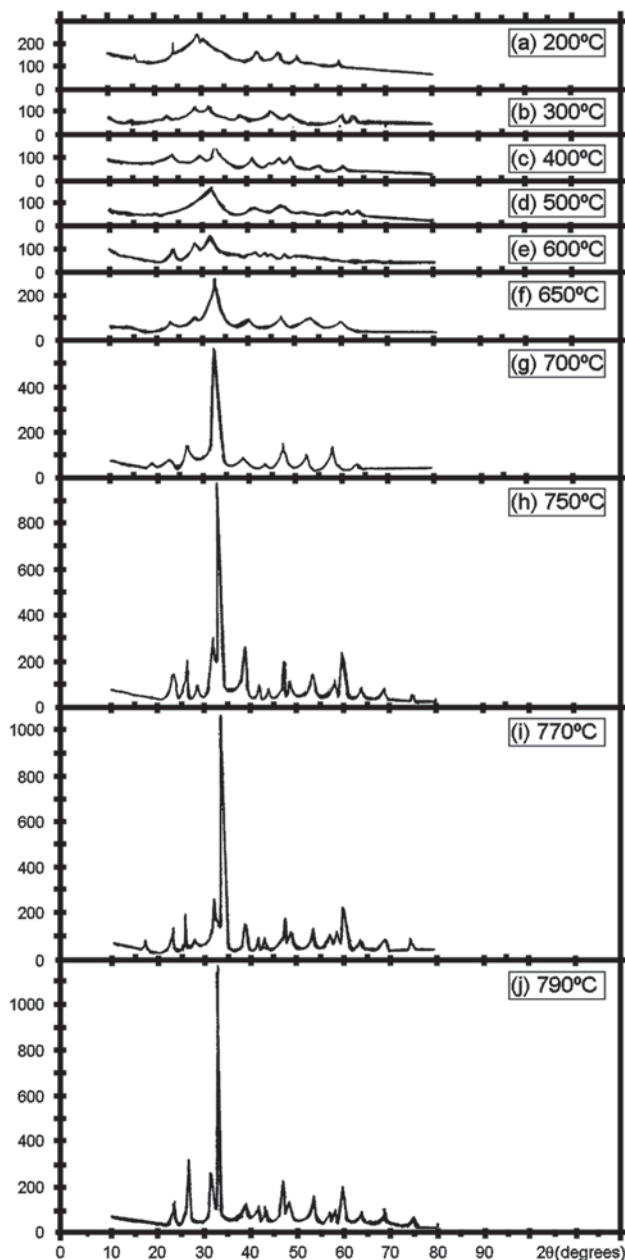


Figure 2. XRD patterns of the yttrium-gadolinium-iron mixed oxide after calcinations at different temperatures

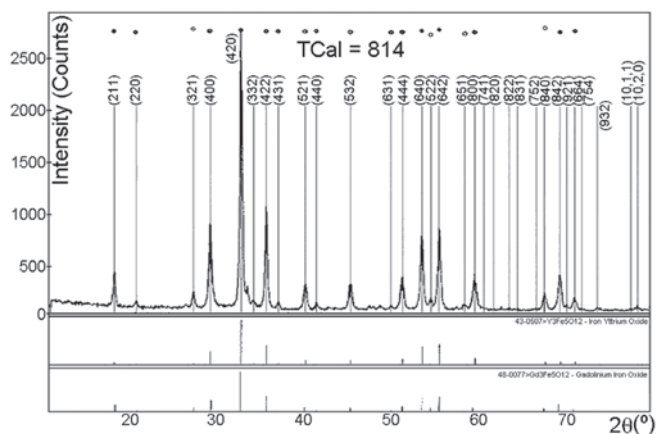


Figure 3. XRD pattern of the yttrium-gadolinium-iron mixed oxide after calcinations at 814 °C

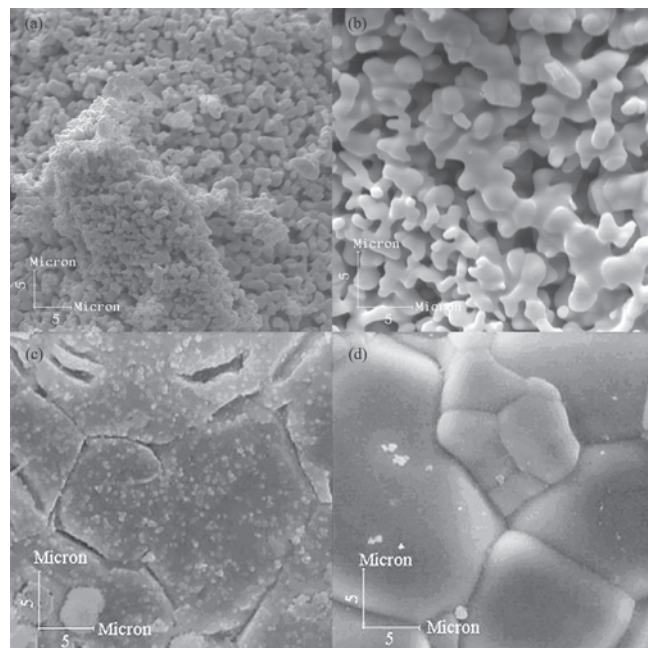


Figure 4. SEM micrographs of: (a) powder calcined at 814 °C; powder calcined at 1200 °C; (c) ceramic ring sintered at 1270 °C; (d) ceramic ring sintered at 1320 °C

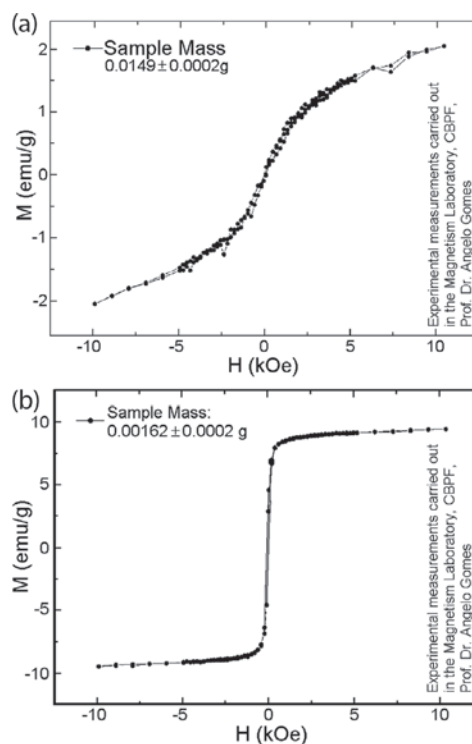


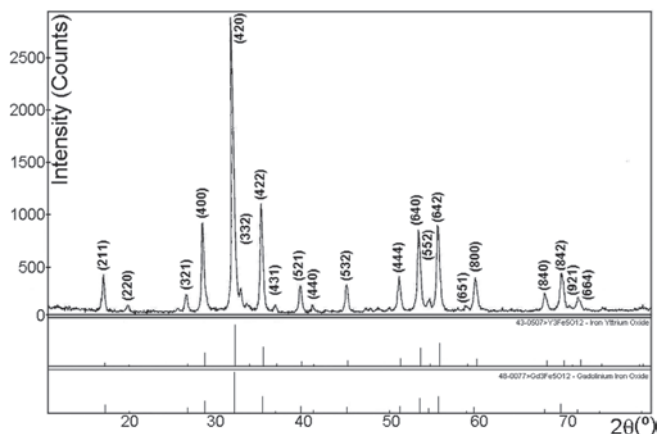
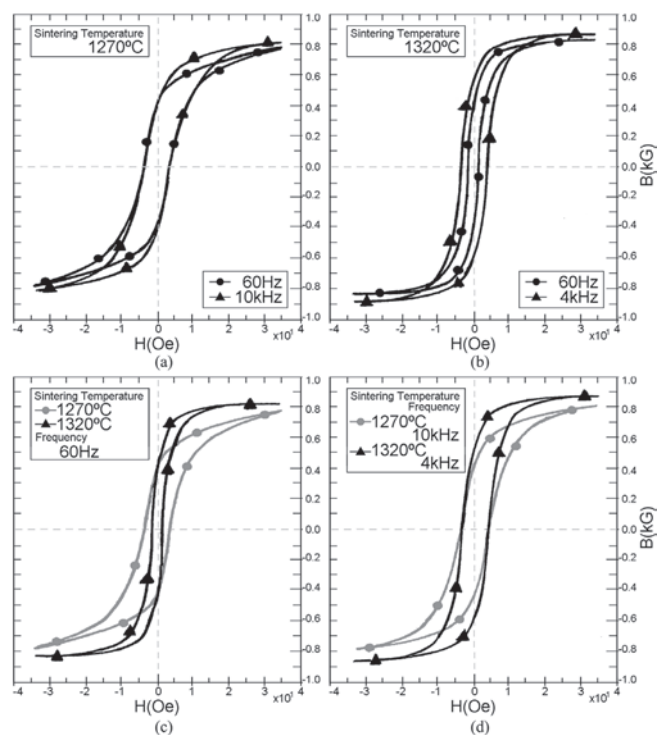
Figure 5. Vibrating Sample Magnetometer hysteresis loop of: (a) powder calcined at 814 °C; (b) milled powder from ceramic ring sintered at 1320 °C

remanent induction, coercive force and hysteresis loss. Table 1 also shows the relationship between density and magnetic properties, arising from difference in the sintering temperature of the YGdIG rings: 1270 against 1320 °C. It is also seen that the coercive force decreases as the sintering temperature increases, because it provides larger grain size and denser rings.

Figure 7 presents the hysteresis loop determined by Walker Scientific

Table 1. Magnetic properties of the sintered GdYIG rings as determined by using Walker Scientific AMH-20 Hysteresisgraph.

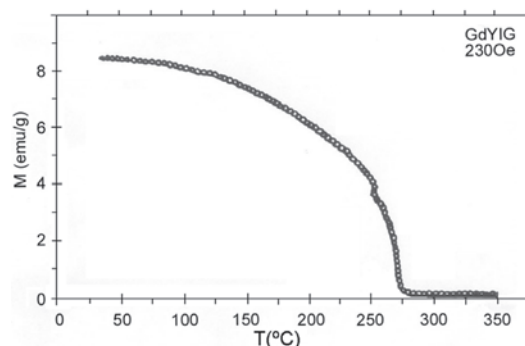
Sintering Temperature (°C)	Grain Size (µm)	% theoretical density	Testing Frequency (Hz)	Coercive Force (Oe)	Saturation Induction (kG)	Remanent Induction	Hysteresis loss (J/m ³)
1270	3.1	87.6	60	2.97	0.79	0.41	86.98
1270	3.1	87.6	10000	3.60	0.80	0.48	112.38
1320	6.5	95.3	60	1.40	0.81	0.34	32.65
1320	6.5	95.3	1000	2.37	0.83	0.43	54.90
1320	6.5	95.3	2000	2.68	0.86	0.47	67.10
1320	6.5	95.3	3000	3.02	0.86	0.51	83.60
1320	6.5	95.3	4000	3.31	0.86	0.53	98.41

**Figure 6.** XRD pattern of the $Y_{1.47}Gd_{1.53}Fe_5O_{12}$ sintered at 1320 °C**Figure 7.** Influence of the sintering temperature and hysteresisgraph test frequency on the shape of magnetic hysteresis-loop of the GdYIG samples

AMH-20 Hysteresisgraph. It is seen that both increase in sintering temperature and test frequency produce easier saturation induction.

In Figure 8 it is seen that Curie temperature is equal to 282.4 °C for $Y_{1.47}Gd_{1.53}Fe_5O_{12}$ studied in this work, a value inside the 272-290 °C range corresponding to those of pure YIG and GdIG²⁸. Also,

Figure 8 shows that saturation magnetization for the considered YGdIG is almost constant at the 34-50 °C temperature range, fitting well what is pointed out by Moulson²⁹ and Harrison³⁰.

**Figure 8.** Graph of saturation magnetization versus temperature for $Y_{1.47}Gd_{1.53}Fe_5O_{12}$

Finally, Figure 5b or Figure 8 together with the density value of the $Y_{1.47}Gd_{1.53}Fe_5O_{12}$ easily allowed to find out the saturation magnetization of this YGdIG sintered at 1320 °C as being equal to 0.17 kG, a value of the same order of magnitude of the values obtained from Walker's Hysteresisgraph measurements (Table 1).

Vella-Coleiro, Smith and Uiter³¹ investigated at 25 °C the radio frequency susceptibility of flux-grown crystals of $Y_{3-x}Gd_xFe_5O_{12}$ in the frequency range 40 to 160 MHz and determined that $4\pi M_s = 0.205, 0.330, 0.740$ and 1.370 kG, respectively, for $x = 2.7, 2.4, 1.8$ and 0.6 . Saturation induction of 0.740 kG for $x = 1.8$ is very similar to that in Table 1 for $x = 1.53$ (0.79 to 0.80 kG for ceramic rings sintered at 1270 °C). Dionne³² provides, per mole, the value $4\pi M$ equal to 1.0 kG for $Y_{1.5}Gd_{1.5}Fe_5O_{12}$ at 300 K (26.85 °C), which is another good fitness.

Patton³³ reported saturation induction in hot-pressed YIG rings from conventional powder mixing method of synthesis as: 1.709, 1.752, 1.755, 1.810 and 1.815 kG for final product's grain-size equal to 1.0, 3.1, 3.4, 9.0, 10.1 µm, respectively. The comparison of these results with those of the present work points out the importance of a higher densification provided by hot pressing (nearly 100% of the theoretical density) while pressure-less sintering provided only 87.6 to 95.3% of the theoretical density in this work.

CONCLUSIONS

The minimum temperature required to convert co-precipitated mixed hydroxides of Y, Gd and Fe to a single phase crystalline $Y_{1.47}Gd_{1.53}Fe_5O_{12}$ is 810 °C, precisely determined by x-ray diffraction patterns, from which it could also be obtained the 12.41243 Å lattice parameter and the density 5.8383 g/cm³ values for $Y_{1.47}Gd_{1.53}Fe_5O_{12}$. The coercive force of $Y_{1.47}Gd_{1.53}Fe_5O_{12}$ decreased with increasing sintering temperature from 1270 to 1320 °C due to grain-growth

and density increase. For sintered rings of $Y_{1.47}Gd_{1.53}Fe_5O_{12}$, increase in test frequency produced increases in maximum induction, remanent induction, coercive force and hysteresis loss. Curie temperature was equal to 282.4 °C for YGdIG of this study. M_s was 9.25 emu/g (0.17 kG), which agreed well with the saturation induction achieved from Walkers's hysteresisgraph loops, whose values fitted well those provided by previously published works.

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REFERENCES

- Prochazka, V. J.; Kohout, J.; Stepankova, H.; English, J.; Kuriplach, J.; Niznansky, D.; *J. Magn. Magn. Mater.* **2004**, 272-276, e1689.
- Kohout, J.; English, J.; Stepankova, H.; Kuriplach, J.; Niznansky, D.; *J. Magn. Magn. Mater.* **2002**, 242-245, 763.
- Kumar, N.; Misra, D. S.; Vankataramani, N.; Prasad, S.; Krishnan, R.; *J. Magn. Magn. Mater.* **2004**, 272-276, e899.
- Takagi, T.; Fujino, M.; Fujii, T.; *J. Cryst. Growth* **2002**, 237-239, 725.
- Joseyphus, R. J.; Narayanasamy, A.; Nigam, A. K.; Krishnan, R.; *J. Magn. Magn. Mater.* **2006**, 296, 57.
- Joseyphus, R. J.; Narayanasamy, A.; Sivakumar, M.; Guyot, M.; Krishnan, R.; Ponpandian, N.; Chattopadhyay, K.; *J. Magn. Magn. Mater.* **2004**, 272-276, 2257.
- Waerenborgh, J. C.; Rojas, D. P.; Shaula, A. L.; Kharton, V. V.; Marques, F. M. B.; *Mater. Lett.* **2004**, 58, 3432.
- Ristic, M.; Nowik, I.; Popovic, S.; Felner, I.; Music, S.; *Mater. Lett.* **2003**, 57, 2584.
- Taketomi, S.; Sorensen, C. M.; Klabunde, K. J.; *J. Magn. Magn. Mater.* **2000**, 222, 54.
- Boudiar, T.; Payet-Gervy, B.; Blanc-Mignon, M. F.; Rousseau, J.; Le Berre, M.; Joisten, H.; *J. Magn. Magn. Mater.* **2004**, 284, 77.
- Tepper, T.; Ross, C. A.; *J. Cryst. Growth* **2003**, 255, 324.
- Kohout, J.; English, J.; Stepankova, H.; Kuriplach, J.; Niznansky, D.; *J. Magn. Magn. Mater.* **2002**, 242-245, 763.
- Cruickshank, D.; *J. Eur. Ceram. Soc.* **2003**, 23, 2721.
- Laval, J. Y.; *J. Am. Ceram. Soc.* **1978**, 61, 455.
- Beregi E.; Hild, E.; Sztanislaw, A.; Rudnay, G.; Sztatisz, J.; *J. Magn. Magn. Mater.* **1984**, 41, 73.
- Music, S.; Ilakovac, V.; Ristic, M.; Popovic, S.; *J. Mater. Sci.* **1992**, 27, 1011.
- Godoi, R. M. H.; Jafelicci Jr., M.; Marques, R. F. C.; Varanda, L. C.; Lima, R. C.; *Quim. Nova* **1999**, 22, 783.
- Cho, Y. S.; Burdick, V. L.; Amarakoon, V. R. W.; *J. Am. Ceram. Soc.* **1997**, 80, 1605.
- Bueno, A. R.; Serra, R. A.; Nobrega, M. C. S.; Ogasawara, T.; *Proceedings of the 41st Brazilian Ceramic Congress, Brazilian Ceramic Association, São Paulo, Brazil, 1997*.
- Reed, J. S. In *Engineered Materials Handbook, Ceramics and Glasses*; Samuels, J.; Schneider, S. J., eds.; Technical Chairman, ASM International, 1991, vol. 4, p. 130.
- Halloran, J. W. In ref. 20, p. 109.
- Malghan, S. G. In ref. 20, p. 65.
- Wu, K. X.; Whitman, D. W.; Kaufell, W. L.; Finch, W. C.; Cumbers, D. I.; *The American Ceramic Society Bulletin* **1997**, 76, 49.
- Pennisi, L. In ref. 20, p. 225.
- Hermansson, L. In ref. 20, p. 135.
- Webb, P. A.; Orr, C.; *Analytical Methods in Fine Particle Technology*, Micromeritics Instruments Corporation, 1st ed., Norcross: Georgia, USA, Chapter 5, p. 9.
- Gilleo, M. A. In *Ferromagnetic Materials*; Wohlfarth, E. P., ed.; North-Holland Publishing Company, 1980, vol.2.
- Moulson, A. J.; Herbert J. M.; *Electroceraics: Materials, Properties, Applications*, 1st ed., Chapman & Hall: London, 1995.
- Harrison, G. R.; Hodges, L. R. Jr.; *Microwave Garnet Compounds, Physics of Electronic Ceramics*, Marcel Dekker: New York, 1972, Chapter 26.
- Vella-Cordeiro, G. P.; Smith, D. H.; van Uitert, L. G.; *J. Appl. Phys.* **1972**, 43, 2428.
- Dionne, G. F.; *J. Appl. Phys.* **1971**, 42, 2142.
- Patton, C. E.; *J. Appl. Phys.* **1970**, 41, 1637.