Influence of Complexing Agents and pH on Yttrium−Iron Garnet Synthesized by the Sol−Gel Method

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A systematic study of the sol−gel technique for the synthesis of $Y_3Fe_5O_{12}$ is presented, using two different complexing agents (citric acid and malonic acid) and adding two different alcohols (ethylene glycol and glycerol). The influence of the pH value of the initial solution on the final product is also studied. Yttrium−iron garnet YIG is obtained from the gels by heating above 650 °C in air atmosphere. Samples are characterized by X-ray powder diffraction and IR spectroscopy. The crystallite size and the lattice parameter are also determined, and their dependence on the synthesis conditions is studied.

Introduction

Yttrium−iron garnet ($Y_3Fe_5O_{12}$, YIG)[1] is the most representative and well-known compound among the rare-earth−iron garnets. This ferrimagnetic material is used widely in electronic devices for the microwave region as well as in magnetic bubble domain-type digital memories.

The most common method for ceramic powder synthesis is the grinding of mixed oxide powders followed by solid-state reactions. However this method requires high reaction temperatures and produces particles with large sizes and a limited degree of homogeneity. Also impurities can be introduced from grinding.

In recent years sol−gel methods have attracted the attention due to the lower synthesis temperatures and the finer and more homogeneous particles produced. However, to achieve the compositional homogeneity of the final oxide powder, the preparation of a homogeneous gel with respect to the distribution of cations is very important. Therefore, a suitable precursor solution must be prepared which can be converted to a gel without any cation segregation.[2]

In sol−gel routes, gelation is frequently attained from solutions of inorganic metal salts and a complexing agent. The concentration of such solutions will produce a homogeneous gel if most of the metal ions are forming chelate complexes. Therefore, the selection of a suitable chelating agent is important, as well as the pH and the concentrations in the precursor solution. Another sol−gel route is the Pechini process.[3] In this method, the precursor solution contains the inorganic metal salts, a chelating agent (citric acid), and a dialcohol (ethylene glycol). Two reactions are involved: an esterification between citric acid and ethylene glycol and complex formation between citric acid and metal ions. The immobilization of metal−chelate complexes in the organic polymer net produced by esterification is expected to reduce segregation of cations.

In this work, we studied the synthesis of YIG from different type of gels: metal−chelate gels and Pechini gels. The aim was the optimization of the sol−gel route for the preparation of YIG. Two chelating agents were selected: citric and malonic acid. The first one was used by Marcilli[4] in the citrate gel process to synthesize a great variety of compounds, included garnets. We prepared citrate gels with different concentrations of citric acid, different initial pH values, and different quantities of ethylene glycol. Furthermore, other gels were prepared using malonic acid as chelating agent. In this case, different malonate gels with and without glycerol were obtained by varying pH according to a modification of the Pechini process reported recently for the preparation of garnets.[5]

Experimental Section

All reactants are reagent grade and were provided by Aldrich. The preparation of the samples is detailed below:

1. Gels C. A solution 0.2 M $Fe(NO_3)_3{\cdot}9H_2O$, 0.12 M $Y(NO_3)_3{\cdot}5H_2O$, and x M ($x = 1, 2, 3$ M) citric acid, was heated at 80 °C in order to obtain the gel. This gel was dried at 110 °C for 36 h and further heat treated in air at temperatures between 400 and 1000 °C and for periods of time between 2 and 24 h, with a heating rate of 10 °C/min.

2. Gels E. A solution 0.2 M of $Fe(NO_3)_3{\cdot}9H_2O$, 0.12 M of $Y(NO_3)_3{\cdot}5H_2O$, and 2 M of citric acid was prepared. Different precursor solutions were obtained by adding some milliliters of ethylene glycol (with molar ratios of citric acid/ethylene glycol in the range 12/88 to 92/8). These solutions were heated with constant stirring until gelation, and then the gels were dried at 110 °C for 36 h. As for gels C, samples were obtained by heating of gels at different temperatures, in air atmosphere.

3. Gels M. An aqueous solution of 0.1 M $Fe(NO_3)_3{\cdot}9H_2O$, 0.06 M $Y(NO_3)_3{\cdot}5H_2O$, and 1 M malonic acid was heated with constant stirring until gelation. This gel was decomposed at 300 °C for 2 h and further heat treated at different temperatures.

4. Gels G. Some milliliters of glycerol were added to a solution 0.1 M $Fe(NO_3)_3{\cdot}9H_2O$, 0.06 M $Y(NO_3)_3{\cdot}5H_2O$, and 1 M malonic acid. Molar ratios of malonic acid /glycerol were over the range 7/93 to 23/78. Gels were decomposed at 300 °C for 2 h and further heat treated at different temperatures.

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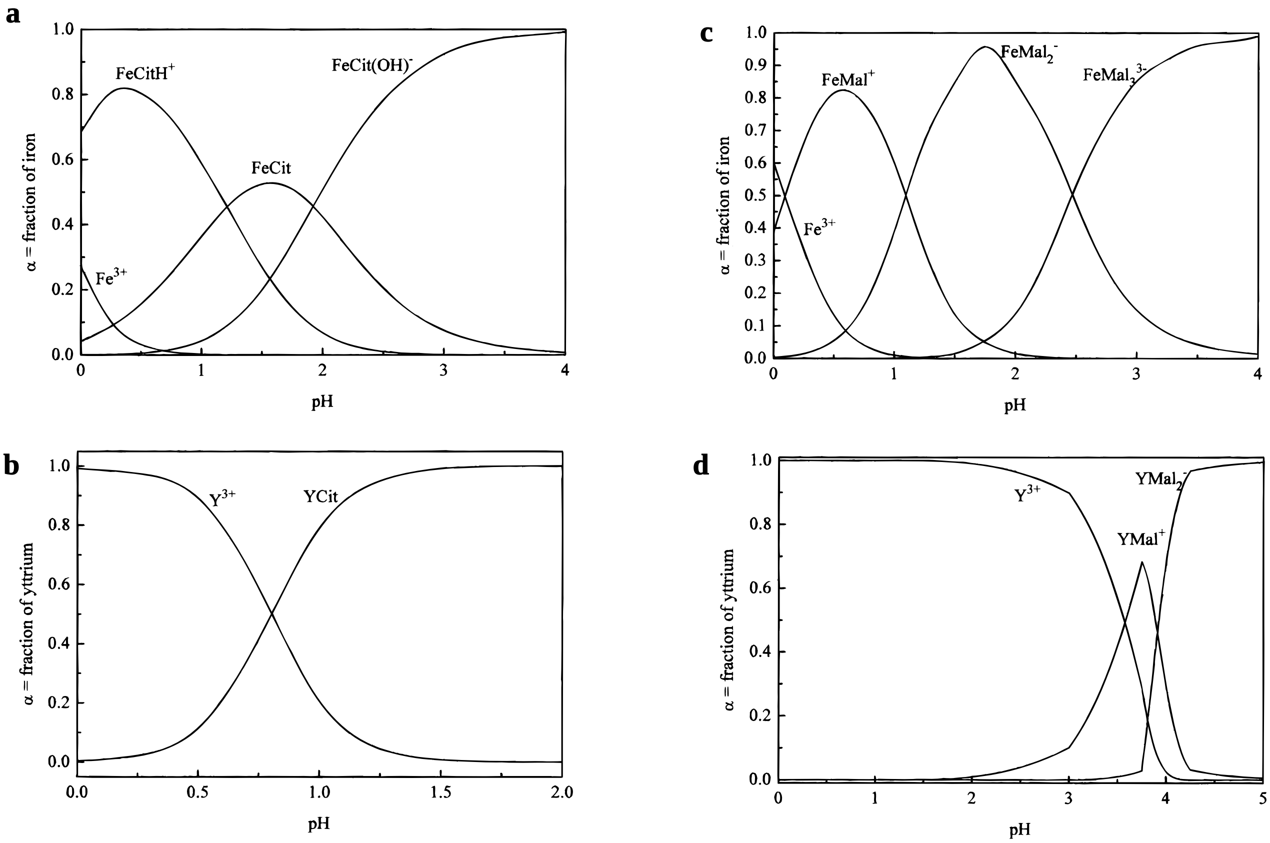

Figure 1. (a) Distribution of iron ions among citrate complexes as a function of pH, for a citric acid concentration of 2 M and an iron concentration of 0.2 M. (b) Distribution of yttrium ions among citrate complexes as a function of pH, for a citric acid concentration of 2 M and a yttrium concentration of 0.12 M. (c) Distribution of iron ions among malonate complexes as a function of pH, for a malonic acid concentration of 1 M and an iron concentration of 0.1 M. (d) Distribution of yttrium ions among malonate complexes as a function of pH, for a malonic acid concentration of 1 M and an yttrium concentration of 0.06 M.

The above-described precursor solutions have low pH values ($pH < 1$). The complex formation reactions depend on the pH, and at such low values, metal ions can be free in solution, not complexed. The stability constants for complex formation reactions are known,[6] therefore, calculations of free and complexed ions as a function of pH were made. Figure 1 shows the species distribution diagrams for iron(III) and yttrium(III) citrate as well as for iron(III) and yttrium(III) malonate. Each curve in these diagrams shows the fraction of metal (plotted vs pH) which forms the complex indicated by the legend of the curve. One can observe that metal ions are wholly complexed above $pH = 1$ with citric acid (H_3Cit) and above $pH = 4$ with malonic acid (H_2Mal). To determine the influence of pH on the process, a solution of NH_4OH was added to some precursor solutions of gels C and M, to adjust the pH to different values. These precursor solutions were heated in the same way as the others. Gels prepared with pH control are listed in Table 1. Preparing citric acid gels at higher pH values is not possible, because precipitation occurs. Thus with citric acid only a gel at $pH = 2$ was prepared.

Samples were characterized with X-ray diffraction (XRD) using a Philips PW-1710 diffractometer equipped with a Cu anode (Cu Kα radiation) and a graphite monocromator. The different phases were identified using the JCPDS Powder Diffration Files.[7] The mean particle size and the microstrains were estimated with the single line method,[8] assuming a Lorentzian shape for the size broadening and a Gaussian shape for the microstrain broadening. Calculations were performed over the line (420). Instrumental width was determined with a YIG specimen prepared by the ceramic method that had large crystallites and was free from defect broadening, and the diffraction peaks were fitted by a pseudo-Voigt function, using the program XRFIT.[9] Lattice parameters were determined with the program XLAT.[10] Infrared spectroscopy measurements were recorded with a Bruker IFS 66 V equipment, from 100 to 4000 cm^{-1}, using the KBr pellet method.

Results and Discussion

Gels C and E before drying are opaque and quite dark in color, but no precipitate can be observed. However, the gel C2 is light green and transparent. Such differences suggest that gels prepared without pH control could have some colloidal precipitate and be less homogeneous. Precursor solutions containing glycerol (gels G) form a precipitate when heated. Instead of a gel, a brown viscous mass is obtained. The role of glycerol is apparently to reduce nitrates causing the precipitation of metals.[11] Thus in this case no polyester resin is prepared. The appearance of gels with malonic acid, prepared at pH values in the range ∼1−6 is similar, and some small quantity of precipitate is formed during gelation. pM′−pH diagrams[12] are useful for avoiding precipitations when designing sol−gel processes, but there is no pM′−pH diagram available for malonic acid. However we know that below $pH = 7$ the pH decreases

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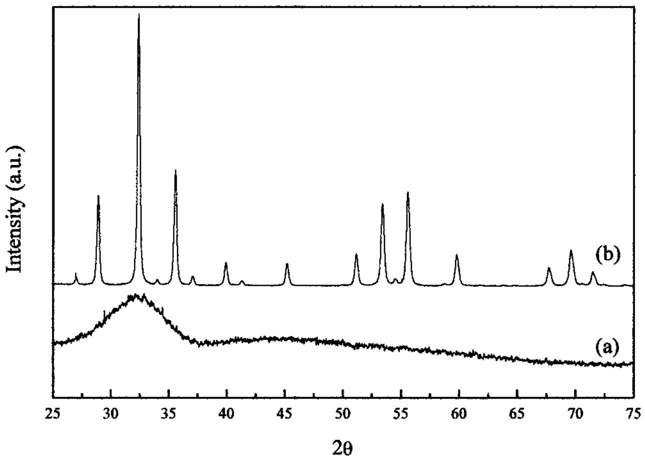

Figure 2. XRD patterns of the samples obtained from gel C2, heat treated at 400 °C (a) and 800 °C (b) for 2 h.

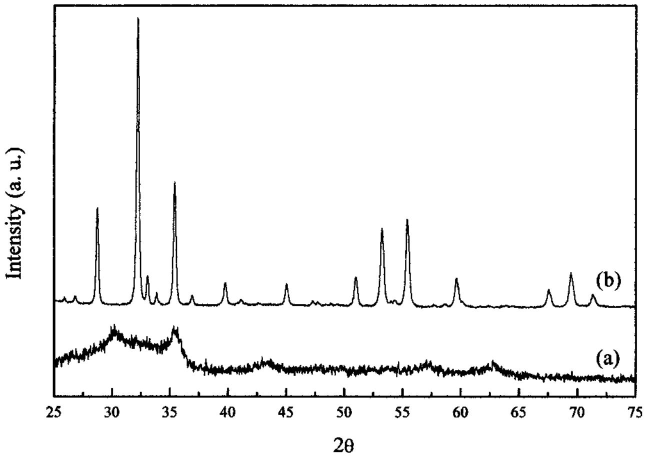

Figure 3. XRD patterns of the samples obtained from a gel E with a molar ratio citric acid/ethylene glycol 27/73, heat treated at 400 °C (a) and 800 °C (b) for 2 h.

Table 1. Gels Prepared with pH Control

gel	composition	pH
C2	citric acid	2
M2	malonic acid	2
M4	malonic acid	4
M5	malonic acid	5
M6	malonic acid	6.4

when the concentration increases, and the precipitation in the malonic gels appears when the initial solution is quite concentrated. As Y^{3+} is not complexed below pH = 4, we can suggest that the precipitation is due to the free Y^{3+} cations.

One can observe on the XRD patterns that samples prepared by heating gels at low temperatures (below 650 °C) are mainly amorphous, but also some weak peaks appear that can be attributed to maghemite (γ-Fe_2O_3) or magnetite (Fe_3O_4). Making a distinction between maghemite and magnetite in these diffractograms is difficult, because the Bragg lines have a low intensity and are very broad. However, XRD patterns of samples prepared from gel C2 do not exhibit any Bragg line, only a broad band characteristic of an amorphous material. We illustrate this in Figures 2−4.

When heated above 650 °C, samples crystallize, and the obtained phases, as well as the rate and the crystallization temperature, depend on the composition of the initial gel. Table 2 shows the different phases determined for the prepared powders.

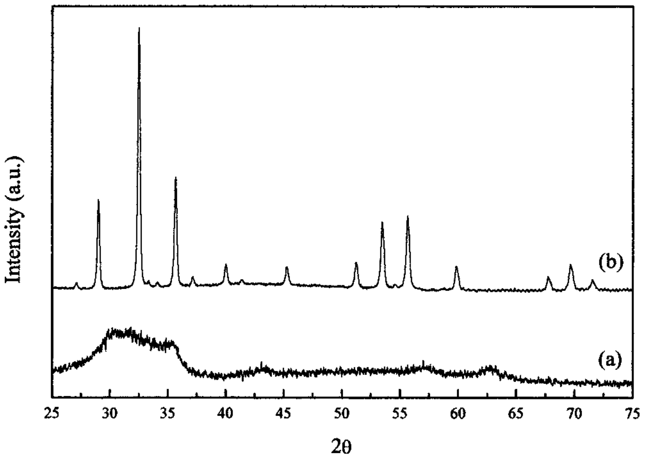

Figure 4. XRD patterns of the samples obtained from a gel G with a molar ratio malonic acid/glicerol 7/93, heat treated at 600 °C (a) and 800 °C (b) for 2 h.

Samples prepared from gels E contain mostly YIG or perovskite, depending on the ratio citric acid/ethylene glycol (see Figure 3). With a high ratio, such as 92/8, the obtained powders contain mostly perovskite ($YFeO_3$). With larger quantities of ethylene glycol in the gel, the perovskite and hematite (α-Fe_2O_3) percentage decreases, but even in the samples prepared with the largest quantity of ethylene glycol (12/88), perovskite and/or hematite are still present. The most intense reflection of $YFeO_3$ appears at 0.2692 nm and the most one of α-Fe_2O_3 appears at 0.2690 nm, so when the percentage of these phases decrease, distinguishing between them is difficult. Gels with ratios over the range 20/80 to 12/88 produce the powders with the lower percentage of perovskite/hematite.

Samples prepared from gels C contain YIG as single phase (see Figure 2). Crystallization occurs at 700 °C or above, and at 700 °C it takes 36 h. Samples prepared from gel C2 contain also YIG as a single phase, but with this gel crystallization begins at 650 °C. This temperature is slightly lower than that required by gels C. Furthermore, crystallization at 700 °C of samples from gel C2 occurs in only 2 h. This lower crystallization temperature could be related with the good homogeneity of the gel prepared at pH = 2. Since this gel does not have any precipitate inside, no maghemite or magnetite appears when the gel is heated below 650 °C, and crystallization can occur at lower temperatures.

Samples prepared from gels G contain mainly YIG, but also small quantities of perovskite and/or hematite, and the crystallization begins at 700 °C (see Figure 4). Samples prepared from gel M contain mainly perovskite and some YIG. With the increase of pH from M2 to M6, the Bragg lines assigned to perovskite decrease and lines assigned to YIG increase (see Figure 5). However, powders prepared from malonate gels contain always some perovskite phase.

From XRD results, one can conclude that malonic acid is not a good complexing agent, and samples prepared from gels containing malonic acid always produce YIG and perovskite. Adding glycerol to these gels yields better results, but instead of gelation, a precipitation occurs. Citric acid seems to be more suitable to prepare gels, but adding ethylene glycol (Pechini route) does not improve the method. Furthermore the pH control of the initial solution leads to a lower crystallization temper-

Table 2. XRD Results of YIG Powders Calcined for 2 h at Various Temperatures[a]

gel	400 °C	600 °C	650 °C	700 °C	750 °C	800 °C	900 °C
C	Am, Fe	Am, Fe		Am > YIG	YIG	YIG	YIG
C2	Am		Am > YIG	YIG		YIG	
E (20/80)	Am, Fe	Am, Fe		Am > YIG	YIG ≫ P	YIG ≫ P	YIG ≫ P
E (92/8)	Am, Fe				P ≫ YIG		
G	Am, Fe	Am, Fe		Am > YIG	YIG ≫ P	YIG ≫ P	YIG ≫ P
M	Am, Fe					P > YIG	
M2	Am,Fe					P > YIG	
M4	Am, Fe					YIG > P	
M5	Am, Fe					YIG > P	

[a] Am, amorphous; Fe, iron oxide; P, perovskite.

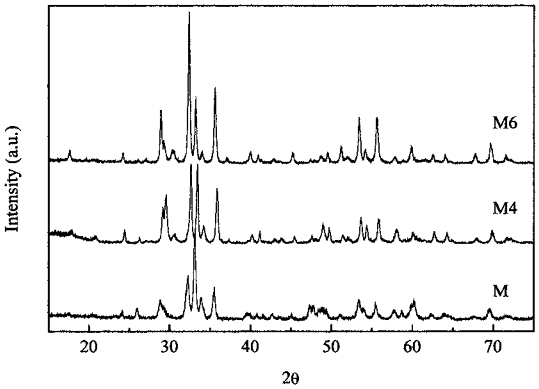

Figure 5. XRD patterns of the samples obtained from malonic gels (M) with different pH values. These samples were treated first at 300 °C for 2 h and further heat treated at 800 °C for 2 h.

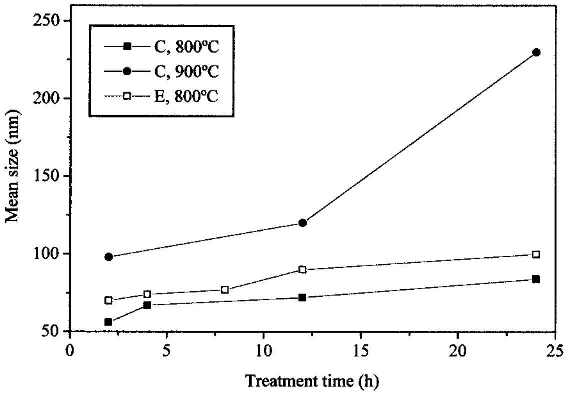

Figure 6. Dependence of the mean particle size on the heat treatment for samples C annealed at 800 and 900 °C, and for samples E (20/80), annealed at 800 °C.

ature. This fact suggests that some precipitation occurs in the gels without pH control. Finally, we can conclude that the best conditions for gelation are those of gel C2. But in order to obtain pure garnets, the atmosphere of the heat treatment is also important.[13] We prepared some samples from a gel C with different treatment conditions: one introducing the gel in the furnace at 800 °C and three samples with a heating rate of 10 °C/min and different atmospheres (nitrogen, air, or without any gas flux). We found that the air atmosphere and a heating rate of 10 °C/min are adequate conditions; increasing the heating rate or using an atmosphere without oxygen produce powders with perovskite and hematite instead of garnet.

To determine the influence of different kinds of gels in the final crystallite size, calculations of the mean size were performed for the crystallized samples containing mainly YIG. Before making the single-line method analysis, Williamson-Hall plots[14] were made, that is, plots of $\beta_f \cos \theta$ vs $\sin \theta$, where β_f is the integral breadth of the deconvoluted function. Such plot gives a line with positive slope if the specimen exhibits microstrain and a nonzero intercept if the specimen exhibits size broadening. Our samples exhibit both a nonzero intercept and a positive slope, therefore broadening is due to size and microstrain effects. From our calculations, we determine that the mean crystallite size varies over the range 30−500 nm, depending on the conditions of the specimen synthesis. The mean crystallite size and the microstrain seem to depend on the annealing temperature as well as on the time treatment. In Figure 6 one can observe that increasing the temperature or the treatment time increased the crystallite size. Furthermore, with both the heat treatment and the treatment time of the samples, the values of microstrain tend to decrease, which is consistent with a better crystallinity of the samples. However, crystallite size and microstrain are quite similar for samples from different gels but with the same treatment. A transmission electron microscopy study was performed on the C samples to determine the particle size,[15] showing a good agreement with the crystallite size estimated from XRD measurements. Thus, one can conclude that every particle contains just one crystallite.

The lattice parameter was determined for all samples that contain mainly YIG. Most of our samples exhibit larger lattice parameters than that of ceramic material (a = 12.3774 Å, JCPDS 33-693) and the lattice parameters values seem to be dependent on the annealing temperature as well as on the time treatment. From Figure 7, one can conclude that the increase in time or temperature of thermal treatment produces garnets with lattice parameters close to that of the ceramic material. The lattice parameter values range from 12.408(1) to 12.3755(3) Å, for samples annealed at 650 and 1000 °C, respectively. The dependence of the lattice parameter with the mean particle size was also studied (Figure 8), and it is concluded that samples with smaller mean particle sizes exhibit larger lattice parameters. Such lattice expansion was also reported for small particles of Ni,[16] hematite,[17] magnetite,[18] or $YFeO_3$.[19]

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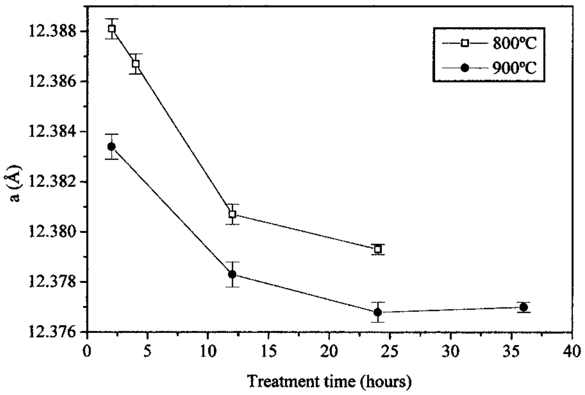

Figure 7. Dependence of the lattice parameter on the calcination temperature and time.

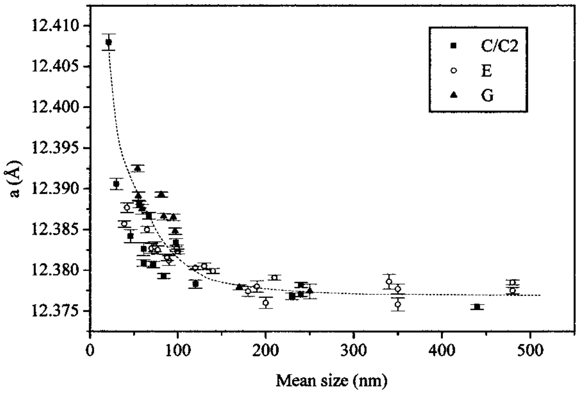

Figure 8. Dependence of the lattice parameter on the mean particle size, for samples prepared from gels C, C2, E, and G.

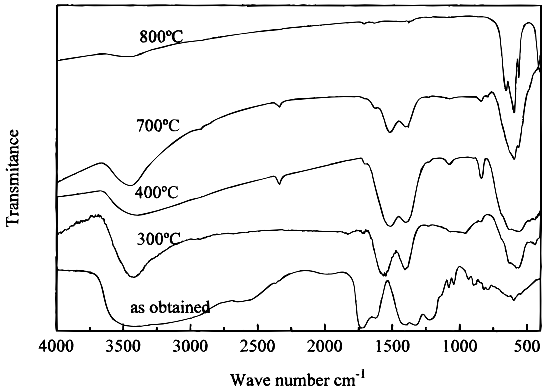

Figure 9. IR spectra of samples C heat treated at different temperatures for 2 h.

However, other small particles, like Pd[20] and Ag,[21] exhibit a lattice contraction, and different models were applied to attempt to explain these phenomena. As a general rule, metal particles usually exhibit a lattice contraction with reduction in particle size, whereas oxide particles exhibit a lattice expansion. For our samples, we found that the lattice expansion of YIG could be explained by oxygen vacancies. In fact, the lattice parameter of the YIG depends on the oxygen vacancies.[22] These vacancies are compensated for by ferrous ions, which have larger ionic radii than ferric ions. Then, with the increase of oxygen vacancies, the lattice expands. However, as pointed out by one of the referees, there is no clear evidence that our samples have any more vacancies than the bulk, and the unit cell expansion with reduction in particle size could result from the increase of the repulsive dipolar interactions at the surface of the particles, due to the existence of unpaired electronic orbitals.[23]

IR spectra of gels C were recorded for the gels as obtained, after drying at 100 °C, and after calcination at 300 °C. As illustrated in Figure 9, two bands appear at 3400 and 1640 cm^{-1} which decrease with drying and calcination and can be assigned to water. In the spectra of the gel as obtained appear three bands at 1726, 1400, and 1200 cm^{-1}, which can be assigned to the vibrations of carboxylic groups. However, the bands at 1726 and 1200 cm^{-1} decrease with the heating procedure and disappear when the gel is calcined at 300 °C. A new band, at 1520 cm^{-1}, together with the one at 1400 cm^{-1}, can be assigned to ionized carboxylates and carbonates[24] resulting from the rupture of citrate molecules. After calcination at 300 °C, a broad band appears also at 565 cm^{-1}, assignable to vibrations of the group Fe–O.

IR spectra of samples heated at 400 and 600 °C exhibit two bands at 1520 and 1400 cm^{-1}, assigned to carbonates. The intensity of these bands decreases with larger treatment time or calcination temperature, but even after 560 h at 400 °C, such bands remain. Two other bands, at 1080 and 850 cm^{-1}, assignable to carbonates, also appear in these spectra. Moreover, there is a broad band at 565 cm^{-1}, assigned to the vibrations of the group Fe–O, and a weak band at 2340 cm^{-1}, assignable to CO_2.

IR spectra of samples annealed at 700 °C exhibit the bands assigned to carbonates, but with lower intensity than before. Furthermore, the broad band at 565 cm^{-1} is replaced by three bands at 660, 600, and 565 cm^{-1}, assignable to the stretching mode of the tetrahedra in the YIG.[25] This result is consistent with the crystallization process observed by XRD around 700 °C. IR spectra of samples annealed above 700 °C do not show any band assignable to carbonates. However, depending on the initial gel, the spectra exhibit only bands assignable to YIG or also some bands that can be assigned to $YFeO_3$.[26] In Figure 10 one can observe the characteristic bands of YIG the spectrum of a sample C annealed at 900 °C.

From IR measurements, one can conclude that the citrate structure is broken down at 300 °C, but some carbonate remains until 700 °C. These results are consistent with those obtained by thermogravimetry.[27] TGA measurements show that the weight decreases sharply up to 400 °C and more slowly up to 700 °C. Above 700 °C the weight loss is negligible.

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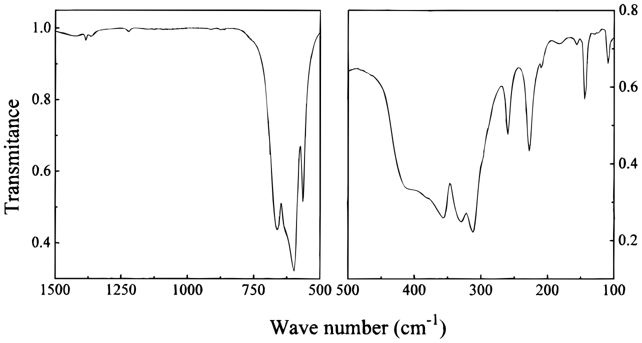

Figure 10. IR spectrum of a sample C heat treated at 900 °C for 2 h.

Conclusions

Yttrium−iron garnet nanoparticles were prepared from different type of gels. A suitable complexing agent, which complexes all the metals in solution, must be selected in order to produce homogeneous gels. If the metals are not complexed, for example using malonic acid, a precipitation occurs and the obtained gels produce powders with a phase mixture. In this work the best results were achieved using a citric gel prepared from a solution of pH = 2. Crystallized YIG nanoparticles were obtained above 650 °C, and depending on the heat treatment, the mean particle size ranged from 30 to 500 nm. Samples annealed below 650 °C are mainly amorphous and contain carbonates. The rupture of citrate molecules occurs around 300 °C, but until 700 °C, some carbonates remain in the powders. Moreover, we observed that a lattice expansion occurs when the mean particle size decreases.

When compared to other wet methods, such as coprecipitation,[28] this sol−gel method leads to yttrium−iron garnet particles which crystallize at lower temperatures (650 °C) and the intermediate compound $YFeO_3$ does not appear. Furthermore, the sol−gel method yields very fine particles.

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