Synthesis of yttrium iron garnet nanoparticles *via* coprecipitation in microemulsion

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We describe a new technique using microemulsions to produce ultrafine precursors of yttrium iron garnet. A coprecipitation of hydroxide or carbonate precursors was made in a W/O microemulsion medium. These precursors (*ca.* 3 nm in size), when heated above 700 °C, transformed to YIG phase. Once prepared, YIG nanoparticles were characterized by X-ray diffraction, transmission electron microscopy and dc magnetic measurements.

Yttrium iron garnet,[1] $Y_3Fe_5O_{12}$ (YIG), is a material used widely in electronic devices for the microwave region as well as in magnetic bubble domain-type digital memories. Some magnetic properties, such as saturation magnetization, remanence and coercitivity, depend critically on the structure and microstructure of the materials. Therefore, it is important to develop techniques to produce garnets with a strict control of the composition, homogeneity, size and particle shape. Also the garnets have a uniquely defined cation distribution and do not present any site inversion problems which can arise in other ferrites; because of this, this kind of ferrimagnetic material is very suitable for magnetism studies.

In recent years, great interest has been focused on the study of the dependence of the physical and chemical properties on the particle size. For this reason, there is renewed interest in the development of new techniques to produce particles of different sizes, sufficiently monodispersed and with a good grade of homogeneity. Water/oil (W/O) microemulsions are ideal media for the preparation of ultrafine particles owing to the small water microdroplets (*ca.* 10 nm) contained inside which, under appropriate conditions, will restrain the growth of the particles. Metal particles and metal oxide particles have been synthesized already by reaction in W/O microemulsions.[2–4] Recently, some mixed-metal oxides have been prepared from oxalate or carbonate precursor particles which were precipitated in microemulsion media: high-temperature superconductors, $YBa_2Cu_3O_{7-x}$, have been synthesized by coprecipitation of oxalate particles;[5] barium ferrite, $BaFe_{12}O_{19}$, was obtained by coprecipitation of carbonate particles,[6] and some perovskites, like $LaNiO_3$, La_2CuO_4 and $BaPbO_3$, were also obtained by coprecipitation of oxalate particles.[7] In this study, we describe the use of W/O microemulsions to obtain $Y_3Fe_5O_{12}$ particles.

Experimental

All chemicals used in this work were reagent grade. $Fe(NO_3)_3 \cdot 9H_2O$, $Y(NO_3)_3 \cdot 5H_2O$, Igepal CA-520 (pentaethyleneglycol monoisononyl phenyl ether), $(NH_4)_2CO_3$ and heptane were provided by Aldrich and aqueous NH_3 by Panreac. Igepal CA-520 is a commercially available non-ionic surfactant which forms W/O microemulsions in the system Igepal CA-520/heptane/water with the concentrations used here (see Table 1). A detailed study of the system Igepal CA-520/decane/water is reported elsewhere.[8]

The precursor to YIG was precipitated from a solution containing iron(III) nitrate and yttrium(III) nitrate, by treatment with ammonium hydroxide or ammonium carbonate. To restrain the growth of precursor particles, a water-in-oil microemulsion was used with Igepal CA-520 as the surfactant, heptane as the continuous oil phase and an aqueous solution as the dispersed phase. Two microemulsions, A and B, with identical compositions but with different aqueous phases were prepared: in microemulsion A the aqueous phase was a solution of iron and yttrium nitrates in stoichiometric ratio, whereas in microemulsion B the aqueous phase was a solution of ammonium hydroxide or ammonium carbonate. Table 1 shows the composition of the prepared microemulsions, and in Fig. 1 the preparation scheme is presented. Table 2 shows the samples prepared and the concentrations of the precipitating agents [aq.NH_3 and $(NH_4)_2CO_3$] used.

Chemical precipitation can be performed by the normal strike method, *i.e.* adding the basic solution to the acidic solution, or by the reverse strike technique, adding the acidic solution to the basic solution. Iron and yttrium ions precipitate at quite different pH values, so better results can be achieved by using the reverse strike technique.[9] The addition of the salt solution to the base results in an almost instantaneous increase of the pH, well above the precipitation pH values of both salts. This will produce more homogeneous precipitates. We used this technique in all cases, adding the microemulsion A into the microemulsion B.

After mixing microemulsions A and B, precursor particles appeared within the aqueous domains of the microemulsion. These precipitate particles were separated in an ultracentrifuge at 5000 rpm for 10 min. The precipitate was washed twice with ethanol and then dried at 80 °C. To obtain the YIG particles, the dried precipitates were calcined at 300 °C for 1 h, then at 400 °C for 1 h and finally annealed at different temperatures.

Before the use of microemulsions with Igepal CA-520 as surfactant, we studied the coprecipitation of YIG precursors in the CTAB/butanol/octane/water system and we observed that it was quite difficult to remove all the surfactant from the precipitate. After 6 washings with ethanol and ethanol–chloroform, we detected the presence of Br^- (from the CTAB) by adding a drop of a solution of silver nitrate to the washing liquid. Because of this problem we changed the composition of the microemulsion and used Igepal CA-520, which can be removed more easily with the thermal treatment of the precipitate.

The hydrodynamic size of the microemulsion droplets was determined from photon correlation spectroscopy (PCS) measurements made with an Ar laser Liconix series ALV-SP80 controlled automatically by means of an ALV-LSE (Light Scattering Electronics) goniometer controller unit. The size and the morphology of the precursors and the annealed samples were studied by transmission electron microscopy (TEM), using a Philips CM-12 instrument. The annealed samples were characterized by X-ray diffraction (XRD), with a Philips PW-1710 diffractometer using Cu-Kα radiation

Table 1 Compositions of the microemulsion systems

	surfactant	oil phase	aqueous phase
microemulsion A	Igepal CA-520	heptane	$Fe(NO_3)_3$ (0.2 mol dm^{-3})+$Y(NO_3)_3$ (0.12 mol dm^{-3})
microemulsion B	Igepal CA-520	heptane	aq. NH_3 or $(NH_4)_2CO_3$
mass fractions	38.13%	53.87%	8%

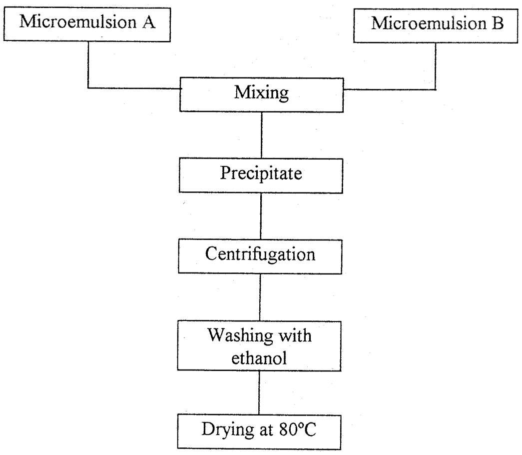

Fig. 1 Schematic representation of the synthesis process

Table 2 Annealed samples

sample[a]	precipitating agent/ mol dm^{-3}	annealing temp./°C	annealing time/h
N1	1.7	600	2
N2	1.7	700	2
N3	1.7	800	2
N4	1.7	800	4
N5	1.7	800	12
N6	1.7	900	2
N7	1.7	1000	2
N8	1.5	800	2
N9	2	800	2
C1	0.6	600	2
C2	0.6	700	2
C3	0.6	800	2
C4	0.6	900	2
C5	0.4	800	2

[a] N, coprecipitation with aq. NH_3; C, coprecipitation with $(NH_4)_2CO_3$.

($\lambda = 1.54186$ Å). The different phases were identified using the JCPDS Powder Diffraction Files.[10] Magnetic measurements were performed using a vibrating sample magnetometer (VSM) model DMS 1660, and hysteresis loops were recorded at room temperature up to 2 kOe.

Results and Discussion

Microemulsion system and precursor particles

The hydrodynamic radius of the microemulsion droplets (without any salt added to the aqueous phase) as determined from PCS measurements was 7 nm. The addition of a salt to the aqueous phase can change the radius values, but we did not make measurements of the size of microemulsions with salts in the aqueous phase because microemulsions containing metal salts are coloured and absorb the light.

After mixing microemulsions A and B, it was observed that the aggregation rate of the particles within the microemulsion depends on the concentration of the precipitating agent, and this rate increases with the increase of the concentration of precipitating agent in microemulsion B.

The washed precipitates were dispersed in ethanol and a drop was deposited on a TEM grid. No differences were observed in the morphology of precipitates with different precipitating agents; for both precipitates the TEM images show aggregates constituted of very fine particles with sizes of *ca.* 3 nm (see Fig. 2).

YIG particles

XRD patterns of the samples annealed at 600 °C exhibit a broad band that can be attributed to an amorphous material, but also some weak peaks appear, attributed to maghaemite (γ-Fe_2O_3), haematite (α-Fe_2O_3) and some small quantity of YIG (see Fig. 3). After annealing at 700 °C for 2 h, XRD patterns show the characteristic peaks of YIG, although the samples are not completely crystallized because the amorphous broad band remains. XRD patterns recorded on samples annealed above 700 °C do not exhibit any broad band. However, depending on the precipitating agent, phases other

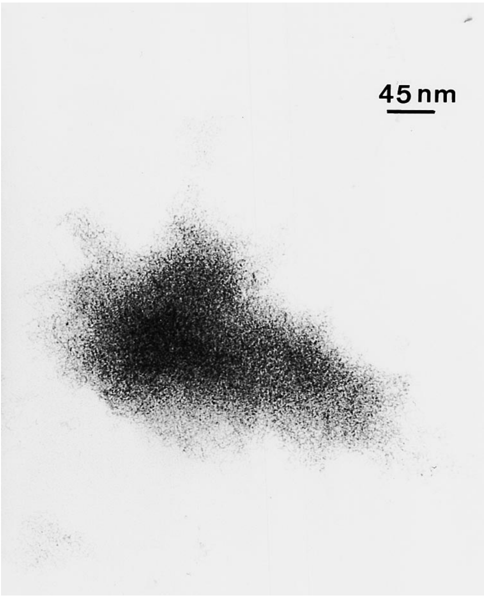

Fig. 2 TEM image showing the precipitate obtained using microemulsion B with 0.6 mol dm^{-3} ammonium carbonate as the aqueous phase

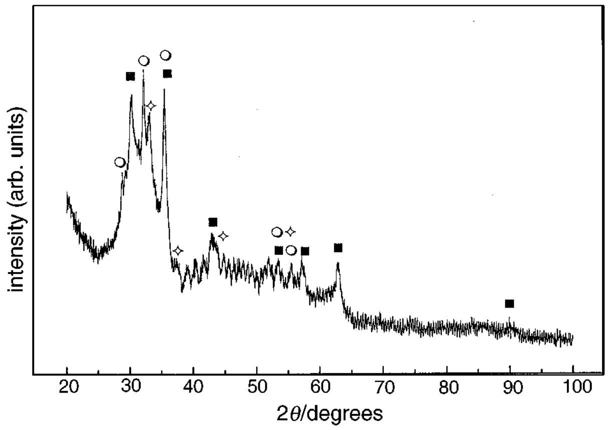

Fig. 3 XRD pattern of the C1 sample (annealed at 600 °C). ■, Maghaemite; ○, YIG; ◇, haematite.

than YIG appear. The diffractogram of the C5 sample [prepared with 0.4 mol dm^{-3} $(NH_4)_2CO_3$] exhibits the lines of YIG, haematite and perovskite ($YFeO_3$; see Fig. 4), and these three phases also appear in the XRD pattern of the N8 sample, prepared with 15 mol dm^{-3} aq.NH_3. The diffractograms of samples synthesized with larger amounts of precipitating agent exhibit only the characteristic peaks of YIG (see Fig. 5).

By coprecipitation of hydroxides or carbonates in an aqueous solution, pure crystalline YIG was produced after heating at 760 °C,[11] so the crystallization temperature does not decrease with the use of microemulsion media. However, for the La–Ni, La–Cu and Ba–Pb oxalate precursors synthesized by Gan *et al.*[7] using a microemulsion technique, a decrease of the crystallization temperature of the samples prepared by the aqueous coprecipitation was reported.

Fig. 6 shows a micrograph of C3 (annealed at 800 °C). Very large aggregates (*ca.* 1 µm) can be observed, which are composed of irregular fine particles. With the increase of the annealing temperature, the particles grow and a sintering process occurs. Crystallized particles are very much larger than precursor particles, as observed also for other mixed oxides synthesized by coprecipitation in microemulsion media.

Fig. 7 shows hysteresis loops recorded at room temperature for the C1 sample, annealed below the crystallization temperature, and for the C3 sample, annealed above this temperature. A marked effect on the magnetization value with the crystallization process is observed. Table 3 shows the values of coercive field, H_c, and magnetization, M_s, measured at 2 kOe for the crystallized samples. The magnetization increases with the annealing temperature, but always remains lower than the bulk value of 26 emu g^{-1}.[12] This discrepancy might be due to the existence of amorphous impurities undetected by XRD or perhaps to the small particle size. However, the magnetization is an intrinsic property of a magnetic material; it is reported that small magnetic particles exhibit lower magnetization values than that of the bulk.[13] The coercive field decreases with the annealing temperature due to the fact that coercitivity depends strongly on the size of the particles, and as observed by TEM measurements, the particle size increases with the annealing temperature.

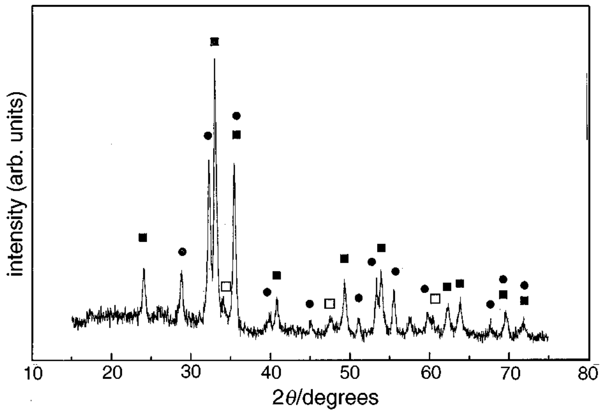

Fig. 4 Diffractogram of the C5 sample, showing the obtained phases. ■, Haematite; ●, YIG; □, perovskite.

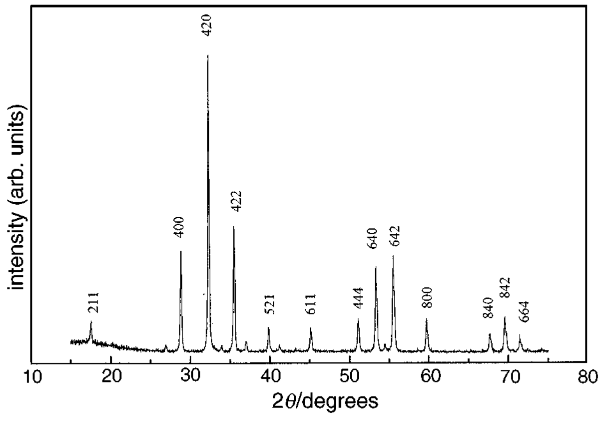

Fig. 5 Diffractogram of the C3 sample (annealed at 800 °C)

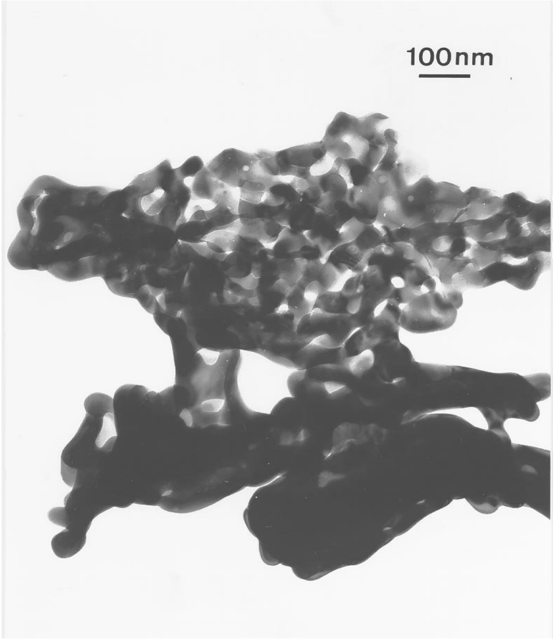

Fig. 6 TEM image showing the morphology of the C3 sample (annealed at 800 °C)

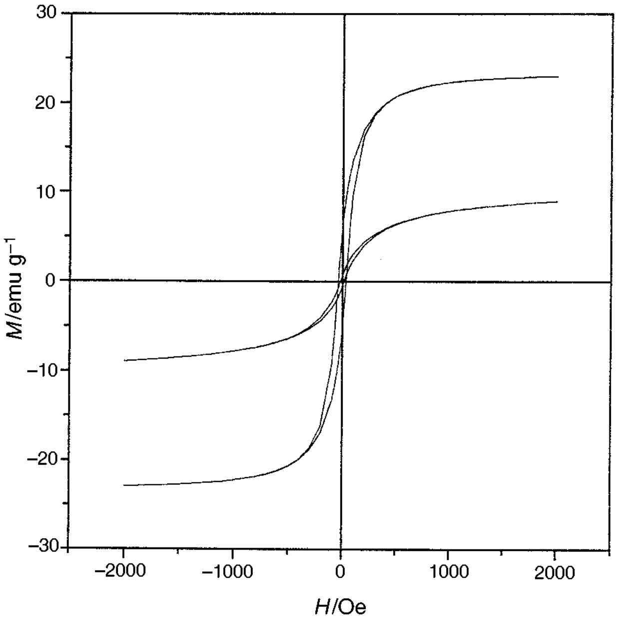

Fig. 7 Hysteresis loops of samples C1 (upper) and C3 (lower) recorded at room temperature

Table 3 Magnetic measurements

sample	M_s/emu g^{-1}	H_c/Oe
N3	21.8	25
N4	21.7	27
N6	22.4	17
N7	23.9	17
C3	23.0	36
C4	24.1	20

Conclusions

A new method for the synthesis of yttrium iron garnet has been developed, using W/O microemulsions as the reaction medium to produce ultrafine precursor particles. These precursors are calcined to produce yttrium iron garnet, as confirmed by XRD and magnetization measurements. The synthesis temperature is 500 °C lower than that for yttrium iron garnet prepared by the conventional ceramic method. This technique can also be applied to other mixed oxide systems.

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