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MAGNETIZATION AND MOSSBAUER SPECTRA OF NON-CRYSTALLINE $Y_3Fe_5O_{12}$

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ABSTRACT

Non-crystalline $Y_3Fe_5O_{12}$ is studied by X-ray, electron microscope, magnetic susceptibility, and Mössbauer effect techniques. The material appears to consist of X-ray amorphous platelets of several microns, which are agglomerations of particles of about 200 Å. Mössbauer spectra at room temperature show Fe in tetrahedral surrounding, while at liquid helium temperature hyperfine splitting for both octahedral and tetrahedral sites is observed. Magnetization measurements show that individual particles order magnetically at ~850 K, much higher than well-crystallized YIG (560 K). These differences are consistent with a high degree of crystallographic disorder and a small particle size. Crystallographic ordering and particle growth are induced by annealing. At 680°C crystalline YIG is formed.

Introduction

A requirement for a fast solid state reaction at low temperatures is the intimate mixing of the constituent materials. Methods as ball-milling freeze-or spray-drying and coprecipitation have been developed in order to meet this requirement for the preparation of complicated oxydes. A variant of coprecipitation is found in the dehydration of a solution of metal-organic salts; pyrolysis of the organic precursor results in a homogeneous mixture from which the desired material can be

prepared, sometimes at suprisingly low temperature (1) .

The present study describes the physical properties of the material obtained by pyrolysis at 400°C of the dehydrated solution of iron citrate, yttrium nitrate and citric acid. The ratio of the metal ions is such that one expects $Y_3Fe_5O_{12}$ (YIG) to be formed at a sufficiently high temperature. Crystalline YIG is indeed formed at 680°C, but the material obtained after pyrolysis already resembles YIG as far as the low temperature ($T \approx 80K$) Mössbauer absorption spectra concern. Electron micrographs reveal platelets with a size of several microns, and the determination of the BET surface area (2) suggests the presence of particles with dimensions of the order of 0.02 μm. The material appears to be X-ray amorphous. The magnetic properties will be discussed within the framework of superparamagnetism. The average magnetic moment per particle and the particle size as deduced from the superparamagnetic behaviour are consistent with the value of the BET surface.

Experimental

The material was prepared in the following way: 13.55 g Y_2O_3 was dissolved in 60 ml 5N HNO_3-solution; 29.00 g Fe(III) citrate (19.26% Fe) and 102 g citric acid were dissolved in 50 ml water. The solutions were poured together, heated to 120°C and kept at this temperature for 12 hours in order to complete the dehydration. Citric acid is added in excess in order to prevent precipitation which might give rise to inhomogeneities. The obtained product was heated at 400°C for 24 hours in an atmosphere of 95% nitrogen and 5% oxygen and again for 24 hours at 400°C in air. Initially the oxygen pressure was kept low in order to prevent a too violent reaction which might lead to local temperatures higher than 400°C. Portions of the obtained material were fired in air at temperatures T_a between 400 and 800°C. No change in weight was observed after these firings.

X-ray diffractograms (Fig. 1), obtained with a Philips diffractometer, only show a broad band between 2.5 and 3.5 Å for

materials which are fired for 4 hours below 680°C. Firing for 4 hours at or above 680°C resulted in a diffraction pattern of YIG, the reflections becoming sharper with higher firing temperature and more prolongated heating.

Electron micrographs show platelets with in-plane dimensions of several microns. The in-plane dimensions do not vary with firing temperature in the range studied (firing from 400-800°C for 4-60 h). Electron diffraction is observed on very thin platelets occurring in materials heated at, or above, 650°C only. Such platelets do not show electron diffraction if $T_a < 650$°C indicating the absence of crystallographic order over a range longer than about 30 Å for the latter samples.

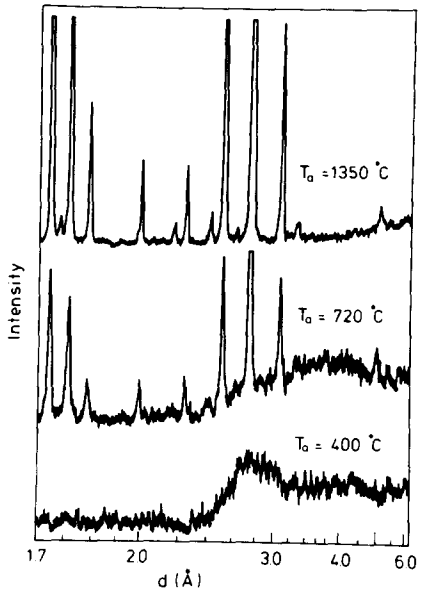

FIG. 1
X-ray diffractograms of samples fired at 400, 720 and 1350°C

The BET-surface (2) was measured with a Leybold-Heraeus Areatron. For materials fired for 4h the specific surface decreases from 53.7 m^2/g for T_a = 400 °C to 39.2 m^2/g for T_a= 680°C. Heating for 60 h at 720°C reduces the specific surface to 3.9 m^2/g.

The magnetization above room temperature was measured by the Faraday method in fields of 1-9 kOe. Below room temperature the measurements were carried out with a recording null coil pendulum magnetometer as described in Ref. 3. The experimental data of the magnetic measurements for the samples fired at 400°C and 720°C are shown in Fig. 2.

The ^{57}Fe Mössbauer spectra were taken at room temperature, liquid-nitrogen and liquid-helium temperature by means of a constant-acceleration spectrometer with a fixed absorber and a moving ^{57}Co in Pd source. For the low-temperature measurements

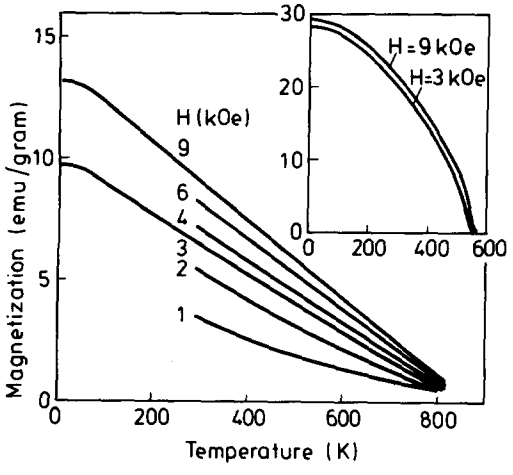

FIG. 2
Magnetization versus temperature in various magnetic fields for the sample fired at T_a=400°C. The insert shows the magnetization for the sample fired at T_a=720°C.

a cold-finger cryostat was used. The absorbers were made of about 100 mg sample mixed with an acetone-based glue and smeared out on Fe-free mica over a circular area of 2 cm dia. The room-temperature spectra of samples fired below 680°C show only a broad paramagnetic ^{57}Fe absorption (line width = 0.90 mm/sec) with a quadrupole splitting $\Delta E_Q \approx 1.1$ mm/sec (Fig. 3). Samples prepared at or above 680°C and below 800°C show a rather broadened spectrum of YIG at room temperature. The tetrahedral ^{57}Fe subspectrum (H_{hf} = 395 kOe) appears to be more broadened than the octahedral one (H_{hf} = 492 and 476 kOe). A similar behaviour is observed in the liquid-helium spectra of the samples fired below 680°C (see Fig. 4). The liquid-nitrogen spectra of the samples fired below 680°C show both a paramagnetic absorption and the onset of a hyperfine splitting. Application of a magnetic field of 3 kOe at room temperature on samples prepared below 680°C results in a broad absorption with a maximum hyperfine field of 280 kOe in addition to the paramagnetic absorption which is present without an applied field.

Discussion

The preparation via dehydration, pyrolysis and firing above 680°C results in the formation of crystalline YIG as can be seen from the properties measured. The magnetic ordering, however, for samples prepared between 680 and 800°C is not yet

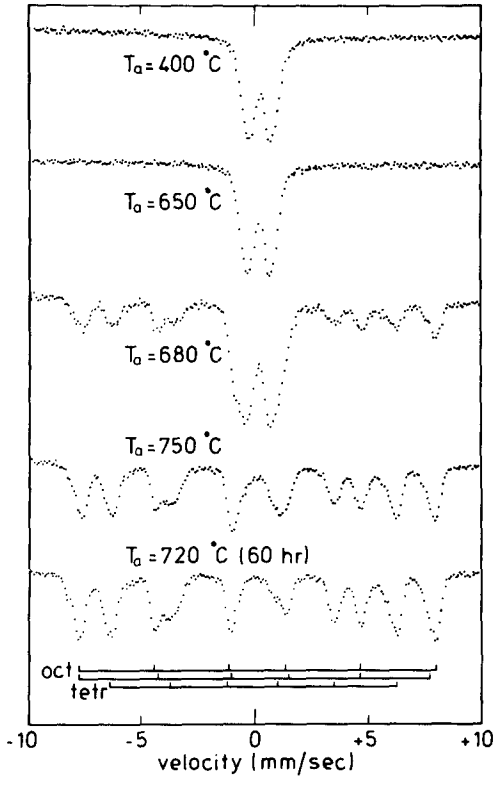

FIG. 3
Mössbauer spectra measured at room temperature for samples fired for four hours at various temperatures. The lowest spectrum was obtained from a sample that was fired for 60 hours at 720°C. At the bottom line positions for octahedral and tetrahedral subspectra as measured in a YIG single crystal are indicated.

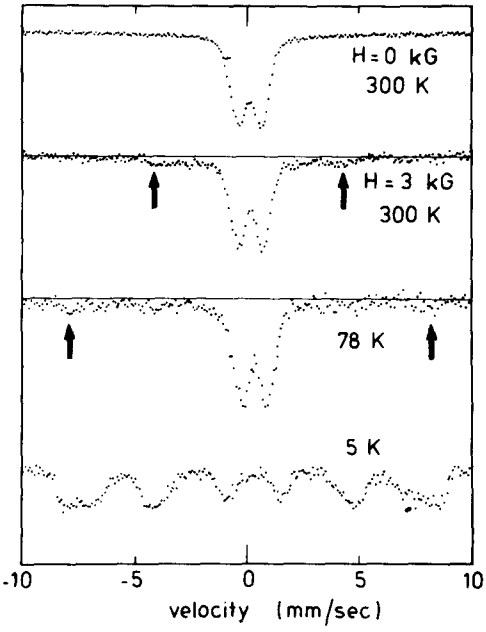

FIG. 4
Mössbauer spectra of the sample fired at 400°C measured at 300, 78 and 5 K. For the 300 K spectrum the influence of an external magnetic field of 3 kOe is given.

comparable to that normally observed in YIG. This can be concluded from both the Mössbauer spectra and the magnetic behaviour. The broadening of the Mössbauer absorption lines especially of the ^{57}Fe tetrahedral absorption indicate that the local ordering is considerably worse than in well-crystallized YIG. The high magnetic field at which the magnetization tends to saturate and the low value of the saturation moment are consistent with this disorder.

Firing below 680°C results in a compound which is X-ray amorphous. The Mössbauer spectra obtained at room temperature are consistent with a superparamagnetic behaviour. This behaviour, however, is better reflected in the magnetic properties as can be found below.

At 5 K a hyperfine splitted spectrum is observed (Fig. 4). Apparently the total particle moment cannot rotate freely anymore at this temperature. The presence of two ^{57}Fe subspectra reveals a close resemblance to normal YIG (4) . ^{57}Fe in α-Fe_2O_3 (5) , γ-Fe_2O_3 (6) or Fe_3O_4 (7) shows quite different spectra. The subspectra are considerably broadened, the tetrahedral ^{57}Fe absorption having the larger broadening. The better ordering of the octahedral ^{57}Fe with respect to tetrahedral ^{57}Fe is almost certainly due to the different numbers of magnetically antiparallel oriented nearest neighbours present. The values of the hyperfine fields at 5 K, 506 ± 20 and 452 ± 15 kOe for octahedral and tetrahedral ^{57}Fe respectively, are somewhat smaller than in polycrystalline YIG (548* and 472 kOe respectively). The reduction of the octahedral ^{57}Fe hyperfine field is larger than that of the tetrahedral ^{57}Fe. This may be explained by different contributions of supertransferred fields to the hyperfine fields of ^{57}Fe at octahedral and tetrahedral positions. Cancelling of supertransferred fields at one position because of magnetic disorder will be proportional to the number of neighbours at the other position. This number is four for the tetrahedral and six for the octahedral site.

The paramagnetic absorption at room temperature for samples prepared below 680°C shows a quadrupole splitting of ~1.0 mm/sec. A splitting of this size has been observed for paramagnetic Fe^{3+} at the tetrahedral position in garnets (8) . Since Fe^{3+} in other oxygen surroundings as e.g. α-Fe_2O_3 (5) and spinel type structures (9) γ-Fe_2O_3 or Fe_3O_4 experiences smaller field gradients we attribute the paramagnetic absorption at 300 K to Fe^{3+} in an oxygen tetrahedron as is found in garnets. There is no reason to assume that field gradients will change substantially because of disorder or the amorphous character of a substance (10) while the size of the particles under

*The geometrical average is taken of the values for the two octahedral ^{57}Fe positions. The two values originate from different contributions of the dipolar field in YIG (see e.g. ref. 4).

consideration (~ 200 Å) is too large to give an increase of field gradients resulting from a large number of Fe-ions with an asymmetrical surrounding at the surface (5) of the particles.

The ^{57}Fe at octahedral positions does not give a sharp absorption at room temperature. This is consistent with the less broadened absorption of the octahedral ^{57}Fe in the room-temperature spectra of samples with $T_a > 680°C$ and in the spectra at 5 K of samples with $T_a < 680°C$. A partial magnetic ordering of a "sublattice" will broaden its paramagnetic absorption. In this context the influence of an external field upon the Mössbauer spectra is of interest. As can be seen in Fig. 4 application of a field of 3 kOe leads to a broad absorption with $H_{hf}(max) \approx 280$ kOe in conjunction with a reduction of intensity in the middle of the quadrupole splitted paramagnetic peak. This reduction suggests that ^{57}Fe nuclei which experience a field gradient smaller than those positioned at tetrahedral sites, are easily ordered by an outer field. Octahedral ^{57}Fe nuclei in paramagnetic YIG show a quadrupole splitting of 0.4 mm/sec (8) and may therefore be responsible for the phenomenon.

The magnetization data of the samples prepared below 680°C can be described assuming superparamagnetic behaviour. In a superparamagnetic system the magnetic moment per particle can reach its average value in a magnetic field within the measuring time by virtue of the small magnetic energy content if the particles are sufficiently small. As a consequence no hysteresis is observed and for sufficiently low anisotropy the magnetization can be described by a Langevin function (see e.g. ref.11)

$$M = Nm(T)\left[\text{cotgh } m(t)H/kT - kT/m(T)H\right],$$

where M is the magnetization, N the number of particles per unit volume, m(T) the magnetic moment per particle at temperature T, and H the applied magnetic field.

The plotting of M vs H at constant temperature indeed results in a curve very similar to a Langevin function for materials prepared at several temperature below 680°C. The magnetization data of these samples can be represented in a

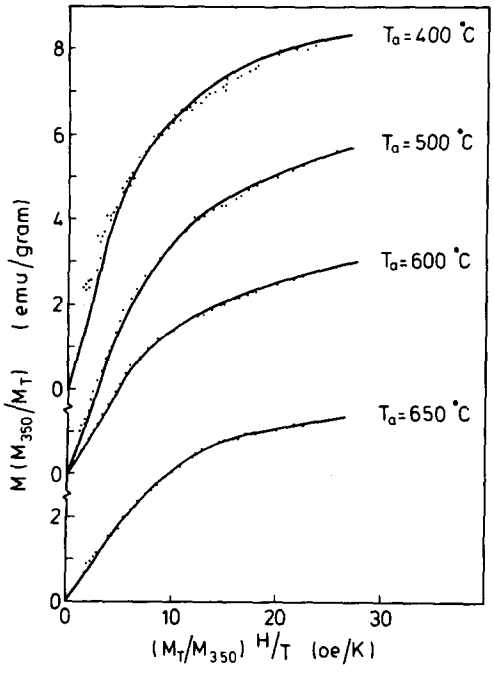

FIG. 5
Reduced magnetization as a function of H/T for samples fired at various temperatures. Drawn curves are Langevin functions.

single curve by plotting $M(M_{350}/M_T)$ vs (M_T/M_{350}) H/T (see Fig. 5), in which M_T is the saturation magnetization at temperature T. Deviations from the Langevin function occur because of a distribution in particle size. The initial susceptibility is very sensitive to the larger particles present whereas the approach to saturation is governed by the smaller particles. As can be seen from the deviations between the measurements and the drawn Langevin curves in Fig. 5 the samples prepared at lower temperatures exhibit a larger width of particle-size distribution. From the fitting of the magnetic data to a Langevin curve we obtain the average magnetic moment per particle m and the effective number of particles N. The results are given in Table 1. From these data we calculate a particle size of about 200 Å. The surface calculated from N is of the same order as the experimentally determined BET surface. Differences between the two values can be explained by the fact that according to electron micrographs we are dealing with platelets of several microns, apparently agglomerations of small particles. Such agglomerations lead to a reductions of the BET surface as compared to the free-particle value. Both the magnetic data and the determination of the BET surface indicate a decrease in number of particles and thus particle growth when heating the sample above 500°C. From the fitting of the Langevin curves at various measuring temperatures to the one curve for a specific firing temperature

TABLE I

Properties of $Y_3Fe_5O_{12}$ annealed at the temperature T_a for t hours. Saturation magnetization M_{350} and average magnetic moment per particle m(350) have been derived from the fitting to a Langevin function (see Fig. 5). The number of particles N has been derived from M_{350} and m(350); the surface from N and the X-ray density of YIG (5.17 g/cm^3) assuming spherical particles. T_o is the apparent magnetic ordering temperature for a single particle. Estimated errors in units of the last decimal place are given in parentheses.

T_a °C	t hours	M_{350} emu/gram	m(350) emu/gram	N 1/gram	surface m^2/gram	BET-surface m^2/gram	T_o K
400	4	9.40 (10)	$3.9(4)\times10^{-17}$	$2.4(3)\times10^{17}$	100(12)	53.7 (5)	920
500	4	8.95 (10)	$3.6(4)\times10^{-17}$	$2.5(3)\times10^{17}$	103(12)		900
600	4	5.85 (6)	$3.2(3)\times10^{-17}$	$1.8(2)\times10^{17}$	91(10)	45.4 (5)	870
650	4	5.45 (6)	$3.0(3)\times10^{-17}$	$1.8(2)\times10^{17}$	91(10)		780
680	4					39.2 (4)	
720	60					3.9 (5)	

(Fig. 5) we obtain the temperature dependence of the magnetic moment per particle. Extrapolation to zero magnetization yields an onset of magnetic ordering at temperatures rather high for iron garnets (see Table 1). However, at these temperatures we observe in the magnetic susceptibility of well-crystallized YIG deviations from the Curie-Weiss behaviour (12), indicating the onset of magnetic clustering. In the present highly disordered materials this onset of clustering is not hindered by well defined long range ferrimagnetic interactions and an increase in "apparent magnetic ordering temperature" can therefore be expected.

Conclusion

The intermediate product after dehydration, pyrolysis and low-temperature firing in the preparation of YIG from an organic precursor has been characterized. From the Mössbauer absorption spectra we conclude that the ^{57}Fe nuclei present in this material, which is X-ray amorphous, occur at positions octahedrally and tetrahedrally coordinated by oxygen, as is found in normal YIG. On local scale the material resembles therefore closely normal YIG. A high degree of disorder and small particle size explain the deviations from well-crystallized YIG. From

the superparamagnetic behaviour of the magnetization a particle size of ~ 200 Å is derived, consistent with the determination of the BET surface. Electron micrographs show that the material consists of plate-like particles with in-plane dimensions of several microns.

Acknowledgements

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