Structure dependence of magnetic properties in yttrium iron garnet by metal-organic decomposition method*

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The yttrium iron garnet (YIG) samples are prepared at different temperatures from 900 °C to 1300 °C by the metal-organic decomposition (MOD) method. The chemical composition and crystal structure of the samples are studied by scanning electron microscope (SEM), XRD, and Mössbauer spectrometer. It is shown that the ratio of ferric ions on two types of sites, the octahedral and the tetrahedral, is increased with the sintering temperature. At 1300 °C, the pure garnet phase has been obtained, in which the ferric ions ratio is 2:3 leading to the minimum magnetic coercivity and maximum saturation magnetization. These results provide a route to synthesize pure YIG materials as the basic materials used in various spintronics applications.

Keywords: yttrium iron garnet, metal-organic decomposition method, Mössbauer spectrometer, magnetic materials

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1. Introduction

Because of the unique magnetic properties, such as small remanence, coercivity, and low intrinsic damping, yttrium iron garnet (YIG) is a significant electronic material used in optical isolators, circulators, modulators, filters, oscillators, and phase shifters, and YIG films have been expected to be the promising material in spintronics studies.[1–4]

The magnetic properties of YIG strongly depend on the chemical composition and crystal structure, therefore it is important to control the stoichiometric quantities, crystallization temperature, and pH to fabricate the crystals.[4–11] Several methods are developed to fabricate YIG and its films, such as liquid phase epitaxy,[5,6] co-precipitation,[12–14] pulsed laser deposition,[1,15,16] sol–gel,[5–8] and metal-organic decomposition (MOD).[12,17,18] The MOD technique, compared to the others, has a lower synthesis temperature as well as some other advantages: uncomplicated, chemical stable, homogeneous, and inexpensive. It is one promising method to conveniently guarantee the synthesis of fine YIG and its films.

However, the synthesis temperatures (T_s) adopted by different research groups using the MOD method to synthesize YIG were quite different,[14,17] varying from 800 °C to 1200 °C. The magnetic properties of the samples, such as saturation magnetization (M_s) and the coercive field (H_c), also changed with T_s. The reason could be that there are $YFeO_3$ and Fe_2O_3 as well as YIG ($Y_3Fe_5O_{12}$) in the products synthesized at the lower temperature, and $Y_3Fe_5O_{12}$ itself has a sophisticated structure, where the ferric ions Fe^{3+} may be on two kinds of sites with different magnetic properties, the tetrahedral and octahedral sites, noted as Fe^{3+} (T) and Fe^{3+} (O), respectively. The only method to determine the ratio of the two different Fe^{3+} located in YIG is the Mössbauer spectroscopy analysis. However, few articles have been applied Mössbauer spectroscopy elaborately in the study of YIG synthesized by MOD.[14,17]

In this paper, we investigate the synthesis process of the YIG by the MOD method crystallized at different temperatures from 900 °C to 1300 °C, verify the component and crystal structure of the YIG powders by scanning electron microscope (SEM), XRD and Mössbauer spectroscopy, and measure the samples' magnetic properties by the vibrating sample magnetometer (VSM). We analyze the ratio of Fe^{3+} (T) to Fe^{3+} (O) in YIG as well as the ratio of $YFeO_3$ and YIG in the samples, and find that the pure garnet phase with outstanding magnetic features, such as the minimum coercivity and maximum saturation magnetization, can be obtained at not lower than 1300 °C by the MOD method. Based on the analysis and discussion, the crystal structure dependence of magnetic properties of the YIG samples is studied thoroughly.

2. Material and methods

The MOD process began with the preparation of a carboxylates solution which contained stoichiometric composition of $Y_3Fe_5O_{12}$. The initial materials were yttrium nitrate ($Y(NO_3)_3{\cdot}6H_2O$), ferric nitrate ($Fe(NO_3){\cdot}9H_2O$), ammonium hydroxide, and propanoic acid.

Yttrium and iron were synthesized to a metal-organic compound with a 3:5 molar ratio by two decomposition

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actions:[19]

$$NH_4OH + C_2H_5COOH \rightarrow C_2H_5COONH_4 + H_2O,$$
$$M(NO_3)_3 + 3C_2H_5COONH_4$$
$$\rightarrow M(C_2H_5COO)_3 + 3(NH_4)NO_3,$$

where M stood for the metal ions. During the process, the pH of the solution was kept to 7.[3,10,11,14]

The YIG powders were prepared firstly by drying the MOD solution at 150 °C for 30 hours. Then the samples were pre-crystallized at 750 °C for 3 hours after grinding in the mortar for several minutes. Finally the ten portions of powders were annealed at 750 °C, 850 °C, 900 °C, 1000 °C, 1050 °C,1100 °C, 1150 °C, 1200 °C, 1250 °C, and 1300 °C for 6 hours, respectively.

An SEM Hitachi S4800 was used to study the morphology and microstructure of the ceramic samples. The components and crystal structures of the YIG powders were characterized by XRD (X'TRA). The ratios of the ferric ions on each kind of site were characterized by ^{57}Fe Mössbauer spectroscopy obtained with a Wissel Mössbauer spectrometer (^{57}Co/Pb) at room temperature. The magnetic properties of the powders were studied using the VSM (lakeshore 7304).

3. Results and discussion

Scanning electron micrographs of the powders by MOD methods calcined at 900 °C, 1100 °C, 1200 °C, and 1300 °C show the change trend of the morphology in Fig. 1. Obviously, the obtained solids below 1300 °C are composed of no regular shaped grains coexisting with prolate spherically shaped particles. The higher T_s leads to the more prolate spherical particles in the samples. It is interesting to note that an almost identical microstructure was observed for the sample synthesized at 1300 °C. Individual particles seem to be a prolate spheroid with a 1 μm diameter and 3 μm length, and partly join each other in Y connection style, which are not like the plate-like crystals synthesized by the sol–gel method.[14,17]

The components and crystal structures of the powders sintered at 750 °C–1300 °C are shown in Fig. 2, characterized in the XRD spectra. According to the XRD patterns, PDF #43-0507, #39-1489, and #39-0238, the sample pre-crystallized at 750 °C comprises just the $YFeO_3$ and Fe_2O_3 phases, without any phases of $Y_3Fe_5O_{12}$. The YIG phase appears in the 900 °C crystallized sample, but its diffraction peaks are weak. Increasing with T_s, the diffraction peaks of the garnet become stronger. Especially, the characteristic peak near 32.3° finally becomes the highest peak as shown in the Fig. 2. While the diffraction peaks of $YFeO_3$ and Fe_2O_3, such as the characteristic peak near 33°, gradually become weaker and finally hard to be recognized when the temperature heightens to 1200 °C. During this process, it is interesting to observe that the colors of garnet samples change from bronzing to khaki and eventually deep green.

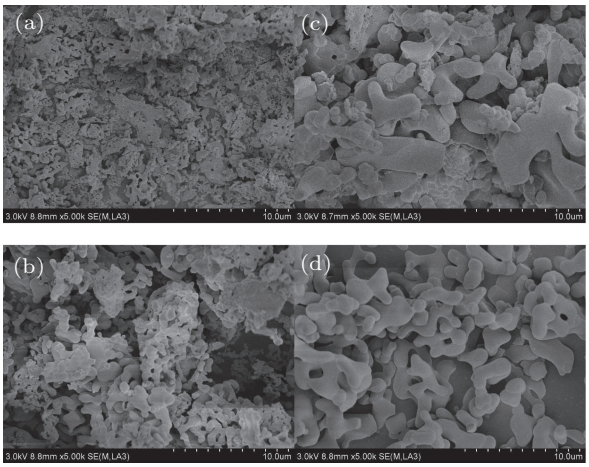


Fig. 1. Scanning electron micrographs of $Y_3Fe_5O_{12}$ synthesized by MOD method at (a) 900 °C, (b) 1100 °C, (c) 1200 °C, and (d) 1300 °C.

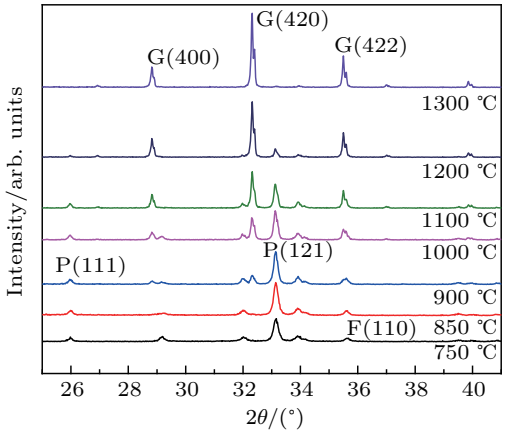


Fig. 2. XRD pattern of the YIG powders sintered at 750 °C, 850 °C, 900 °C, 1000 °C, 1100 °C, 1200 °C, 1300 °C. F, P, and G stood for the Fe_2O_3, $YFeO_3$, and $Y_3Fe_5O_{12}$, respectively. It would be noticed that each peak due to YIG splits into two peaks due to Cu-Kα_1 and Cu-Kα_2.

The crystallization process in MOD has been deduced as the following two steps:

$$Y_2O_3 + Fe_2O_3 \rightarrow 2YFeO_3,$$
$$3YFeO_3 + Fe_2O_3 \rightarrow Y_3Fe_5O_{12}.$$

However, the temperature at which the reactions carry on until $Y_3Fe_5O_{12}$ is thoroughly synthesized has not been confirmed in the MOD method, which is popularly considered to be lower than that in the other solid state reaction methods.[17,20,21]

Here, the process at different temperatures is verified from the ^{57}Fe Mössbauer spectroscopy shown in Fig. 3. The sextet with an internal field (H_i) of 51.59 T belongs to well crystallized α-Fe_2O_3. Another sextet with H_i of 49.71 T belongs to perovskite structured yttrium orthoferrite $YFeO_3$. The doublet corresponds to small α-Fe_2O_3 particles, which was born out of the collapse of α-Fe_2O_3 sextet due to superparamagnetic relaxation.[22] The total atomic ratio of Fe in both types of α-Fe_2O_3 is 55% calculated from the fitting parameters (Table 1). As the annealing temperature is elevated to 850 °C, the total atomic ratio of Fe declines to 42%.

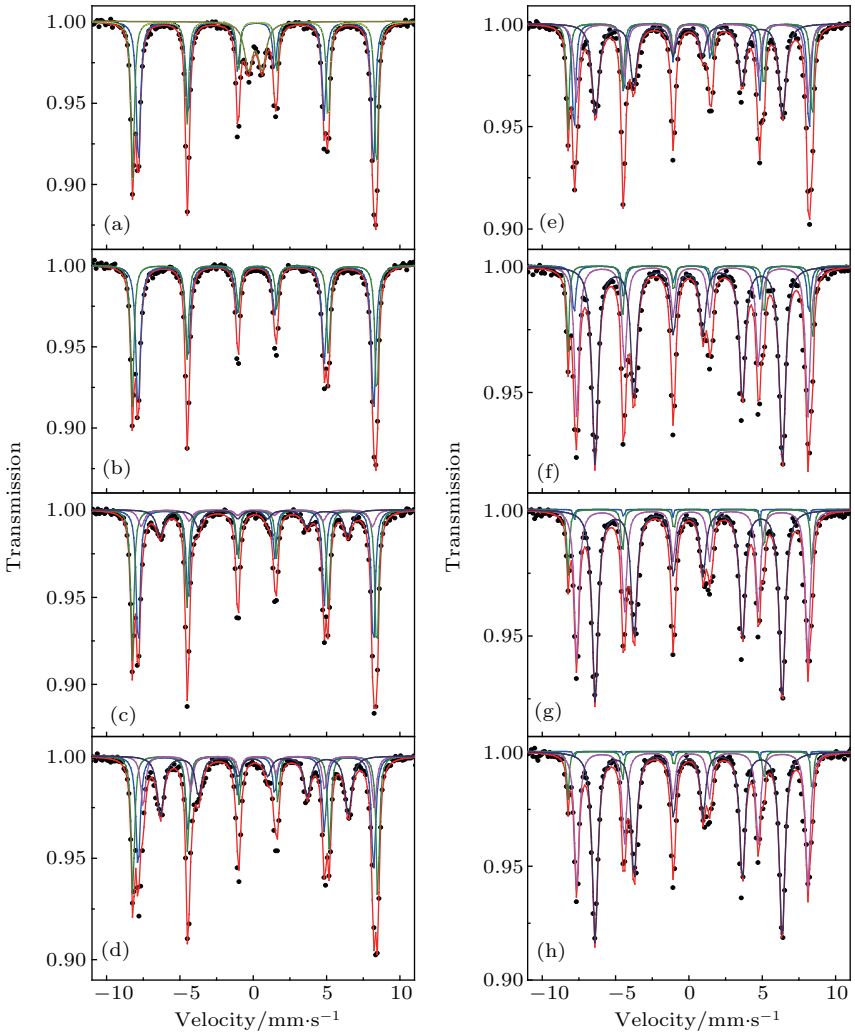


Fig. 3. Mössbauer spectroscopy of sample annealing at (a) 750 °C, (b) 850 °C, (c) 900 °C, (d) 1000 °C, (e) 1100 °C, (f) 1200 °C, (g) 1250 °C, and (h) 1300 °C.

As T_s is elevated to 900 °C, a new sextet with a field of 39.70 T appears in the spectra. Its isomer shift and quadrupole splitting value are identical with the Fe^{3+} on the tetrahedral sites of the YIG.[23] In the binary system of Y_2O_3–Fe_2O_3 with a little excess of Y, the reaction product tends to be a mixture of $YFeO_3$ and YIG instead of non-stoichiometry YIG.[24] Therefore, we deem that YIG is formed as the sample sintered at 900 °C, as judged also from the XRD pattern where the diffraction peaks of YIG appear in Fig. 2.

The sextet of corresponding Fe^{3+} ions occupying octahedral sites in YIG has a superposition with the sextet of Fe^{3+} ions in $YFeO_3$. As the octahedrite of FeO_6 in $YFeO_3$ and YIG have the same structure and much the same bond length,[25] Mössbauer spectrums of the two types of Fe^{3+} ions exhibit approaching resonance absorption peaks. Hence, we divided the superposed sextet into two sub-spectrums with H_i of 49.7 T and 48.9 T for $YFeO_3$ and octahedral sites occupied Fe^{3+} in YIG as shown in Fig. 3(b).

With the increasing of annealing temperature, the changes of isomer shift, quadrupole splitting value, and hyperfine field indicate that $YFeO_3$ transforms to YIG. It is clear to see that the YIG sample reaches 95% purity when T_s is 1300 °C. More importantly, the ratio of Fe^{3+} (O) to Fe^{3+} (T) within YIG may not strictly meet to 2:3 as a result of a different recoil-free factor at a different lattice, which means the pure YIG powders have the fine crystal structure.

Figure 4 shows the room temperature magnetic hysteresis loops of the powders sintered at different temperatures. The samples sintered at the temperatures lower than 1000 °C are too rough to form the hysteresis loops, so the figure does not include the curves of them. It is clear that the samples are soft magnetism and saturated when the magnetic field is applied over 1000 Oe, therefore the *M*–*H* loops have been taken just up to 0.2 T. As seen in Fig. 5, following the T_s, M_s increases from 10.4 emu/g to 29.7 emu/g which is just near to the theoretical value of 30 emu/g, and H_c decreases from 47 Oe to 5.5 Oe. It is easy to understand that these magnetic properties are dependent on the annealing temperature as the compositions and crystal structures are different at various temperatures, which can be comparably seen from the XRD pattern (Fig. 3) and Mössbauer spectroscopy (Fig. 4).

Table 1. The fitting parameters of Mössbauer spectra.

Temperature/°C	Sample	Area	I. S./mm·s^{-1}	H_i/T	Q. S./mm·s^{-1}	W/mm·s^{-1}	Temperature/°C
750	YIP	0.45	0.19	0.37	49.71	–0.02	0.32
	Fe_2O_3	0.41	0.20	0.37	51.59	–0.20	0.26
	Fe_2O_3	0.14	0.14	0.31		0.93	0.65
850	YIP	0.58	0.19	0.37	49.83	–0.01	0.36
	Fe_2O_3	0.42	0.20	0.37	51.72	–0.21	0.27
900	YIP	0.39	0.19	0.37	49.75	–0.02	0.29
	Fe_2O_3	0.38	0.19	0.37	51.72	–0.20	0.27
	YIG-O	0.08	0.22	0.40	48.92	0.06	0.53
	YIG-T	0.15	0.00	0.18	39.70	0.09	0.60
1000	YIP	0.31	0.19	0.37	49.82	–0.02	0.34
	Fe_2O_3	0.29	0.25	0.43	51.82	–0.22	0.26
	YIG-O	0.15	0.34	0.52	48.92	0.06	0.37
	YIG-T	0.25	0.03	0.21	39.75	0.10	0.55
1100	YIP	0.22	0.19	0.37	49.71	–0.02	0.26
	Fe_2O_3	0.19	0.19	0.37	51.66	–0.21	0.24
	YIG-O	0.23	0.20	0.37	48.90	0.06	0.40
	YIG-T	0.37	–0.03	0.15	39.57	0.07	0.54
1200	YIP	0.05	0.19	0.37	49.71	–0.02	0.17
	Fe_2O_3	0.10	0.19	0.36	51.69	–0.21	0.21
	YIG-O	0.33	0.20	0.38	48.90	0.05	0.38
	YIG-T	0.52	–0.03	0.15	39.63	0.04	0.49
1250	YIP	0.01	0.19	0.37	49.71	–0.02	0.07
	Fe_2O_3	0.09	0.19	0.36	51.61	–0.21	0.21
	YIG-O	0.35	0.20	0.38	48.90	0.06	0.38
	YIG-T	0.55	–0.03	0.15	39.58	0.03	0.47
1300	YIP	0.01	0.19	0.37	49.71	–0.02	0.08
	Fe_2O_3	0.06	0.19	0.36	51.70	–0.22	0.18
	YIG-O	0.36	0.20	0.38	48.90	0.07	0.38
	YIG-T	0.57	–0.03	0.14	39.58	0.02	0.44

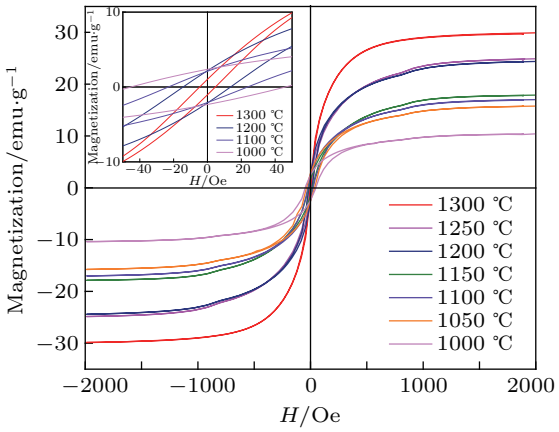


Fig. 4. Room temperature hysteresis loops of powders sintered at 1000 °C, 1050 °C, 1100 °C, 1150 °C, 1200 °C, 1250 °C, and 1300 °C. The low magnetic field parts of the curves are indicated as an inset figure to make clear the change of coercivity.

In Refs. [14] and [17], it had been mentioned that the main reason of the M_s and H_c changing with the annealing temperature was that the particle size became smaller as the temperature was raised. However, based on the measurements and analyses above, we deem that the exact reason is correlated to the morphology, composition, and the crystal structure, especially the iron ions ratio. M_s of YIG powders closely depended on the quantity of Fe^{3+} ions distributed in the octahedron and tetrahedron, which formed two coupled antiferromagnetic structures. The theoretical ratio of the ions on the two sites is 2:3 in the perfect YIG crystal structure, leading to the maximum M_s. The ratio is gradually achieved with the T_s increased, actually revealed from the Mössbauer spectroscopy in Fig. 3. As for the gradually diminishing H_c, it can be explained qualitatively: when the particles become homogeneous prolate spheres and the crystal structure becomes more and more perfect as the T_s goes up as shown in Figs. 1 and 2, the shape-induced anisotropic demagnetizing fields of the grains, as well as crystal defect numbers, porosity, and internal stress in particles, reduce step by step until the pure garnet phase, with the minimum H_c by MOD methods, has been obtained at 1300 °C.

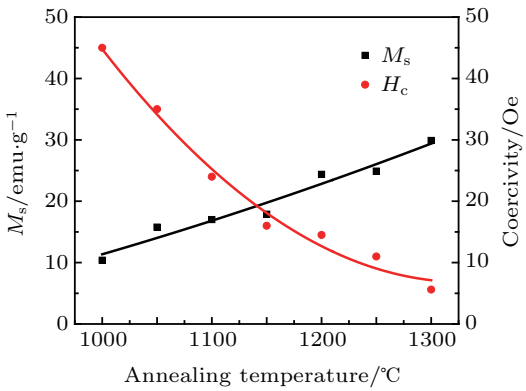


Fig. 5. Saturation magnetization and coercivity dependence of the annealing temperature at 1000 °C,1050 °C, 1100 °C, 1150 °C, 1200 °C, 1250 °C, and 1300 °C.

4. Conclusion

YIG powders are prepared by the MOD method at different crystallized temperatures from 900 °C to 1300 °C. The chemical composition and crystal structure of the samples are studied by SEM, XRD, and Mössbauer spectroscopy. The YIG phase is formed as the sample sintered at 900 °C, and the pure YIG is obtained at the temperature over 1300 °C. It is shown that the ratio of the number of ferric ions on the octahedral sites to those on the tetrahedral sites gradually conforms to the theoretical value 2:3 as the sintering temperature increases. The right iron ions ratio in the YIG sample leads to the smallest magnetic coercivity and highest saturation magnetization, which is significant and useful for the devices research based on pure YIG materials.

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