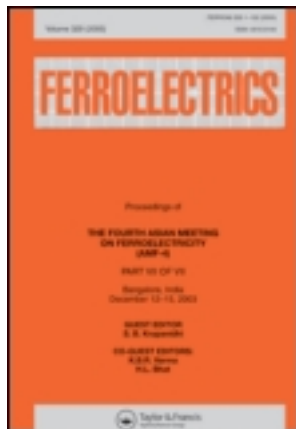


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## PREPARATION AND ANNEALING PROCESS OF $Y_3Fe_5O_{12}$ BY SOL-GEL METHOD

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Yttrium iron garnet (YIG) powders were prepared by sol-gel process. The synthesis parameters including pH values, molar ratio, reactive temperature and time and annealing treatment were studied for formation reaction of single phase YIG. The transformation of precursor to gel and to crystalline phase were determined by differential thermal analysis (DTA), thermogravimetric analysis (TGA), and X-ray powder diffraction (XRD). The results showed that pure phase YIG powders could be obtained through sol-gel process by controlling the relevant annealing process.

**Keywords:** Yttrium iron garnet; Formation reaction; Sol-gel; Annealing treatment

### INTRODUCTION

$Y_3Fe_5O_{12}$  (YIG) is one representative of materials with garnet structure, which is frequently used as isolators, circulators, and magneto-optical devices for its excellent soft magnetic properties at microwave frequencies and optical frequencies<sup>[1-3]</sup>. YIG ceramic is usually prepared from starting materials  $Fe_2O_3$  and  $Y_2O_3$  by solid-state reactions with extensively mechanical mixing and long time heat treatments above 1300 °C. These processing conditions do not allow facile control over microstructure, grain size and grain size distribution in the resulting powders. Coprecipitation route is employed as an alternative method for preparing YIG nanocrystals<sup>[4]</sup>, but single phase YIG is very difficult to be obtained. Sol-gel is a widely used technique involving atomic scale mixing and enhanced reaction rate, which provides the possibility of homogenous nucleation of magnetic particles<sup>[5,6]</sup>.

The performance of the magnetic materials with garnet structure has a strong relationship with its particle size, shape and morphologies. A typical example is that when the particle size is smaller than the critical dimension, superparamagnetism will govern the magnetic

properties<sup>[6]</sup>. Sol-gel has shown some advantages in forming well-dispersed nanocrystals and uniform distribution<sup>[5]</sup>. A recent study showed that the coercivity values for YIG ceramic prepared by sol-gel process was enhanced in comparison with that by conventional route. It appears very important to control the formation reaction for single phase YIG.

The objective of this paper is to well understand the transformations of precursor to gel and to crystalline phase during the formation of YIG powders. It is found that single-phase YIG powders could be obtained through sol-gel process by well control the experimental conditions.

## EXPERIMENT

All chemical reagents used in our experiments are analytical grade. The chemicals,  $Y(NO_3)_3 \cdot 5H_2O$  and  $Fe(NO_3)_3 \cdot 9H_2O$  were used as the starting materials. Citric acid was employed as chelator. Stoichiometric mixture of nitrates of iron (III) and yttrium (III) was dissolved in an aqueous solution of citric acid. The mixed solution was stirred for several hours until the solution becomes transparent and dark red. Then a given concentration of ammonia solution was added dropwise with magnetic stirring to adjust the pH to 2, at which the maximum of iron (III) and yttrium (III) were chelated with citric acid as calculated by critical stability constants theory<sup>[8,9]</sup>. The solution became light yellow-green. The transformations of precursor sol to gel were completed by drying at constant temperature water-bath of 80 °C. The gel showed very viscous and transparently deeply yellow-green. The gels were dried by putting into constant temperature cabinet at 110 °C for 36 h to get deeply black powders. The powders were then put into ceramic crucible for annealing at different heating rates and different temperatures in air.

The structures of all specimen were identified by means of powder-X-ray diffraction (XRD) on a Rigaku, D/max- $\gamma$  A, 12 kW XRD diffractometer with a rotation target and Ni-filtered Cu  $K\alpha$  radiation at room temperature. The scan rate was  $10^\circ 2\theta$  /min. The phase transformation of the dried gel was analyzed by DTA-TGA in air with a TA Instruments thermal analyzer mode TA2000. The heating rate of DTA and TGA was 10 °C/min.

## RESULTS AND DISCUSSION

### **Influence of water quantity on the formation of single phase YIG**

The YIG powders could be obtained in a sequence of the dissolution of nitrates and citrate acid, the formation of precursor sol, polymerization of sol and heat treatment. It was found that besides the influence of citrate acid on the cascade-ionization, the formation rate of gel, water quantity and annealing temperature determined the purity of garnet phase. In order to examine the influence of water quantity on phase structure of the final products, citrate acid with different concentration (1-3M) was selected for comparative experiments. Three samples were obtained by these conditions. Figure 1 shows the powder XRD patterns of these samples.

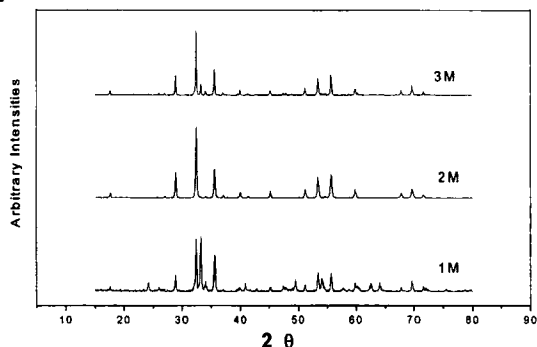


FIGURE 1. XRD Patterns of the samples of certain quantity of citrate with different molar concentration: 1 M, 2 M, 3 M

For 1M citrate acid, since the water quantity is relatively more and less to join in polymerization, the time of constant temperature water-bath at 80 °C to form gel would delay. During the concentration of gel, some of citrate acid with little iron (III) and yttrium (III) would loose, and this would cause the departure of stoichiometry from the initial ratio of the reactants. As revealed by XRD patterns in Figure 1, the final product was a mixture with  $\text{Fe}_2\text{O}_3$  as the main phase.

For 3M citrate acid, the sol became not very clearly but its viscosity was enhanced. The latter factor increased the difficulty for the reactants to react completely. Although the time of constant temperature water-bath at 80°C to form gel was shortened, the inhomogeneity of the components of the gel would be increased so as to make the temperature required in the following annealing treatment increase. From the XRD patterns of the 3 groups of comparative experiments, we can see that when the citrate acid concentration was 2

M, a single phase YIG was obtained.

### **Influence of pH values on the formation reaction of YIG**

The quantity of the citrate acid used in the reaction depended on the quantity of metal ions in the solution with the proportion 1:1. We can use adequate more citrate acid (2 M) than the coordination reaction stoichiometry in our experiments in order to make more metal ions react.

Since the results of the coordination reaction depend on the pH value, we use  $\text{NH}_3 \cdot \text{H}_2\text{O}$  to adjust the pH value of the solution. The pH value of the precursor sol was usually less than 1.0 before adjustment. However, in our experiment, the strong acidity gets most of the metal elements existed as free ions which were the unwanted phases, and this also has influence on the following annealing treatment. In our experiment, we found that with the same annealing treatment dealing with the dry gel obtained from the sol with different pH value, the granularity and fluidness of powders were different too. But only were metal ions chelated with citric acid as more as possible, the pH of solution would be adjusted to 2.

### **Structure transformation from gel to single phase YIG**

Figure 2 shows the DTA-TG curves for the dry gel in air at a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$ . From the DTA curve, there were two strong exothermic peaks at  $285$  and  $337\text{ }^\circ\text{C}$ , which were attributed to the thermal decomposition of the organic components and nitrate species<sup>[5]</sup>.

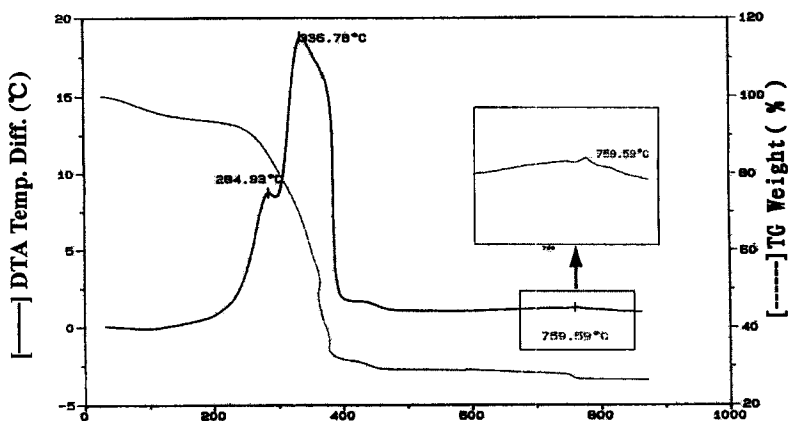


FIGURE 2. DTA and TG curves of the dried gel for YIG prepared by sol-gel method

Accordingly, a great weight loss was observed in TG curve with a total weight loss of ca. 60 %. The weight loss lasts up to 460 °C, indicating that the thermal decomposition persisted only less intensely than the same reaction before 337 °C. At 760 °C there is a weak thermal effect, which could be understood by analyzing local zoom of the curve. The dome begins at 500 °C with a maximum at 760 °C. From the XRD patterns, we found that YIG crystalline formed at 650 °C, we can deduce that the dome is the crystalline peak of YIG. No obvious weight losses were observed in TGA curve after 460 °C, indicating all organic components were decomposed.

Annealing temperature and heating rate accounted for the grain growth and particle shape of YIG. All samples were kept at the setting annealing temperature for 2h and then naturally cooled. As shown in Figure 3, when the annealing temperature increased from 650 to 800 °C, the main peak of the samples enhanced gradually; while from 800 to 900 °C, the intensity of the main peak changed slightly. The results indicate that in the temperature between 650 and 800 °C, YIG was formed with the disappearance of the impurity phases. At 800 °C, the formation reaction for YIG was completed, thus between 800 and 900 °C the intensity of the peak didn't boost up.

The heating rate affects the structure and the size of YIG crystals.

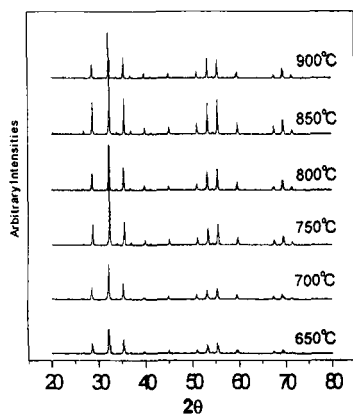


FIGURE 3. XRD patterns for YIG powders annealing treatment at different temperature: 650°C, 700°C, 750°C, 800°C, 850°C, 900°C

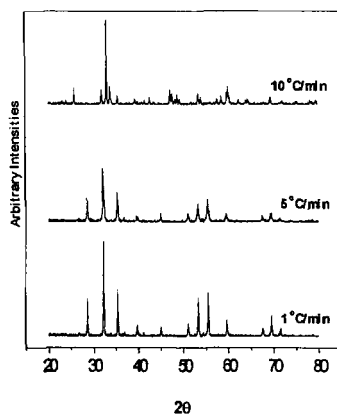


FIGURE 4. XRD patterns for different heating rate: 1°C/min, 5°C/min, 10°C/min

As shown in Figure 4, at the same annealing temperature, a higher heating rate gave much more impurity phases. From this, we can suppose the oscillatory relationship between the purity of YIG phase and the heating rate. The reason is probably that when the heating rate is rather high, the reaction between iron (III) and yttrium (III) could not form the structure of YIG due to some thermodynamic restraint, so the products are mixtures. We found that using suitable annealing conditions, it is possible to prevent the impurity phases during the formation reactions. The higher heating rate lead to smaller particle size, while more impurity phases were present. On the contrary, the lower heating rate gave bigger particle size. A good solution to this problem is only to choose a compromise method, that is under the premise of the purity of YIG phase assured, we could increase the heating rate as high as possible.

## CONCLUSIONS

1. The quantity of the citrate acid used in the reaction depended on the quantity of metal ions in the solution in principle. We can use adequate more citrate acid than the coordination reaction stoichiometry for reaction with more metal ions involving. The results of the coordination reaction depend on the pH value.
2. In the annealing treatment, the temperature and the heating rate are the two key factors which influence the structure and size of the final products. The peak of YIG crystalline is a slow exothermic dome which began at 500 °C.

## ACKNOWLEDGMENTS

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