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# The effect of precipitate agent in co-precipitation synthesis $Y_3Al_5O_{12}$ and $Y_3Fe_5O_{12}$ powders

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**Keywords:** Co-precipitation; YAG; YIG; Precursor powder; Dispersion

**Abstract.** The YAG and YIG powders have been prepared by co-precipitation technique in which $NH_4HCO_3$ or $(NH_4)_2CO_3$ is used as a precipitant and $Y(NO_3)_3{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ as raw materials. The composition, the phase formation process and the properties of the YAG and YIG powders were investigated by means of XRD, SEM, TEM and EDS. The results indicated that the precipitant effects the preparation of pure-phase powders. The resultant YAG and YIG powders showed good dispersity and excellent sinterability using AHC as precipitant.

## Introduction

Yttrium aluminum garnet (YAG) with the chemical composition $Y_3Al_5O_{12}$ has been well established as a laser host material [1-2], attributed to its relatively stable lattice structure and large thermal conductivity [3]. And yttrium iron garnet ($Y_3Fe_5O_{12}$, YIG) is one of the most important ferrimagnetic materials and has been widely applied for tunable microwave devices, circulators, isolators, phase shifters, nonlinear devices, etc. attributed to its excellent electromagnetic properties, including low dielectric loss, narrow ferromagnetic resonance line width in microwave region and tailorable saturation magnetization. In the YAG and YIG garnet structure, space group Ia3d, the yttrium ions occupy the special position 24c, with dodecahedral coordination, the aluminum ions (YAG) or the iron ions (YIG) occupy the special 24d sites, with tetrahedral coordination and the 16a position with octahedral coordination, and all oxygen ions are in the general 96h position [4].

YAG and YIG have been successfully prepared over the entire composition range by solid-state reaction method, with $Y_2O_3$, $Fe_2O_3$ and $Al_2O_3$ as raw materials, in which a relatively high temperature (>1400°C) and prolonged heating time are required [3, 5]. However, solid-state reaction method has some unavoidable disadvantages, such as the processing conditions fail to allow for easy control of microstructure, grain size or shape of the resulting powders. In recent years,

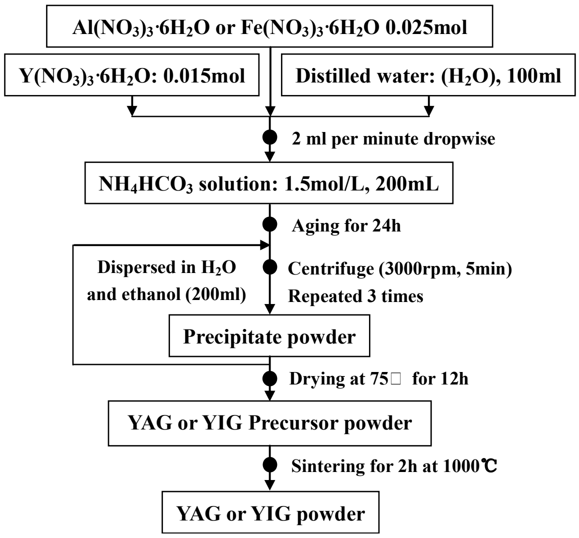


**Figure 1.** Schematic representation of the preparation process of $Y_3Al_{5-X}Fe_XO_{12}$ particles synthesized by co-precipitation method.

with the development of science and technology in the field of materials, a number of wet chemical synthesis methods have been developed and successfully used for the preparation of YAG or YIG nano-sized powders, such as the sol–gel method, hydrothermal synthesis, spray thermal decomposition and metal-organic preceramic processing. These chemical processes achieve symmetrical mixing on the molecular level, lowering the crystallization temperature. Unfortunately, most of these chemical methods suffer from complex and time-consuming procedures and possible mismatch in the solution behavior of the constituents.

Compared with these methods, co-precipitation method is a relatively simpler and more cost-effective way for powder synthesis [6], because precursor powders can be prepared on a large scale in water rather than in organic chemicals, without using special apparatus. However, YIG prepared by co-precipitation method usually used NaOH or $NH_4OH$ as precipitant, but YAG used ammonium hydrogen carbonate (AHC) as precipitant, because of the $Al(OH)_3$ amphotericity. In this work, we have prepared YAG and YIG nano-powders by co-precipitation method, the effects of precipitant have been described. Ammonium hydrogen carbonate (AHC) and ammonium carbonate (AC) was used to synthesize YAG and YIG powders from a mixed solution of aluminum, iron and yttrium nitrates via co-precipitation method. Phase evolution of the precursors and sinterability of the resultant powders were investigated and compared with the different methods.

## Experiment

Compounds of composition YAG and YIG were prepared by co-precipitation method in this study. As starting materials, weighted amounts of $Y(NO_3)_3 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ (A.R., Tianjin Fine Chemicals) with molar ratio of 3:5 for $Y^{3+}$: ($Al^{3+}$ or $Fe^{3+}$) were first dissolved in 100mL deionized water, and the concentrations of mother solution were 0.15M for $Y^{3+}$. Then the mixtures were added drop-wise into the precipitant solution at a speed of 2ml per minute and under vigorous stirring at room temperature (27˚C). In this work, ammonium hydrogen carbonates (AHC), and ammonium carbonates (AC) were used as precipitating agents, and were analytical grade. The precipitation processes were made by the reverse-strike method (adding the mixed salt solution to the precipitant solution). The precipitated slurry was aged for 24 h to make the reaction sufficient, and then the suspensions were filtered and washed repeatedly with distilled water and ethanol to remove residual ammonia and nitric ions. After washing, the resulting product was dried at 75˚C for 12 h, and then the loose precursors were obtained. Finally the precursors were sintering at 800-1100˚C in air atmosphere for 2 h. The preparation process is schematically shown in Fig. 1.

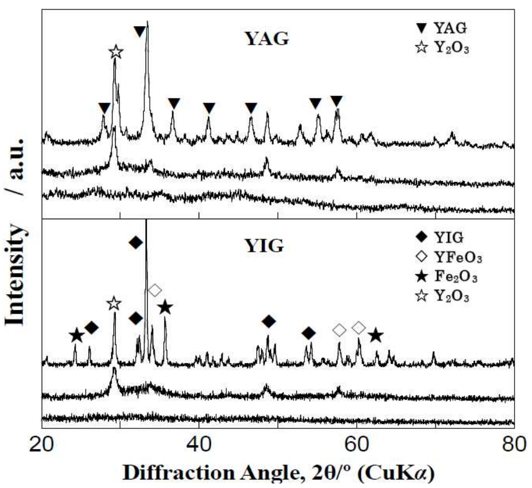


**Figure 2**. The XRD patterns of the dried powders synthesized with $(NH_4)_2CO_3$ sintering for 2h at (a) precipitate, (b) 600℃, (c) 1000℃, respectively.

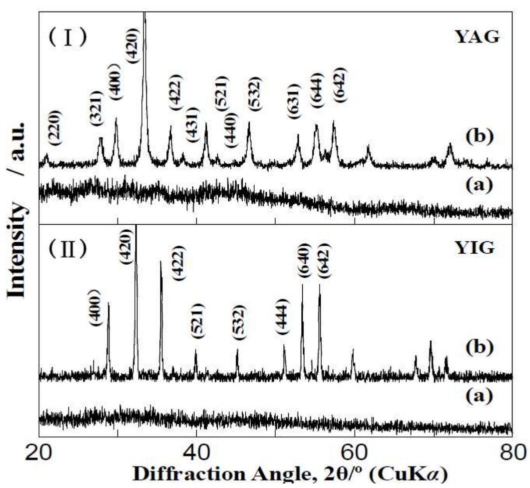


**Figure 3**. The XRD patterns of the dried powders synthesized with $NH_4HCO_3$ sintering for 2h at (a) precipitate, (b) 1000℃, respectively.

The phase identification was performed by using a conventional D/max X-ray diffract meter with Cu-$K\alpha$ radiation in the range of $2\theta$=20~80°. The morphology of the powders annealed at different temperature for 2 h after being ultrasonically dispersed in ethanol was observed by the transmission electron microscope (TEM) and HRTEM. The elemental composition can be determined with a Link ISIS energy dispersive X-ray spectrometer (EDS).

## Results and discussion

**The effect of precipitate agent.** YIG prepared by co-precipitation method usually used strong caustic solutions such as NaOH or $NH_4OH$ as precipitant, but prepared YAG usually used ammonium hydrogen carbonate (AHC) as precipitant, because of the $Al(OH)_3$ segregation in strong caustic solutions. So in this experiment, we examined the effect of different precipitant in co-precipitation method for the YAG and YIG powders.

Fig. 2 shows the XRD patterns of the YAG and YIG powders produced by the AC method sintering for 2h at (a) precipitate, (b) 600˚C, (c) 1000˚C, respectively. For the YAG powder as shown in Fig.2 (I), amorphous YAG was found at 600˚C with the presence of cubic $Y_2O_3$ crystallized peaks. At 1000˚C, YAG phase formed, but the $Y_2O_3$ cubic phase persisted and the intensity unchanged. This suggests that the precursor produced by the AC method contains excess $Y_2O_3$. It is considered that a segregation of $Al^{3+}$ could happen; make the ratio of $Y^{3+}$ and $Al^{3+}$ deviate from 3:5 in co-precipitated powders; thus, some $Y_2O_3$ phases appeared in the calcined powder. However, for the YIG powders produced by this method as shown in Fig.2 (II), YIG phase also can been formed at 1000˚C, but the $Y_2O_3$ cubic phase persisted and a mixture of $YFeO_3$, $Fe_2O_3$ and $Y_2O_3$ has been observed. This suggests that the synthesis of YIG precursor is more complex than YAG. These differences can be attributed to the higher difficulty to precipitate the $Fe^{3+}$ than the $Y^{3+}$ used ammonium carbonates (AC) as precipitating agents during the synthesis

Fig.3 shows the XRD patterns of the YAG and YIG powders produced with AHC method sintering for 2h at (a) precipitate, (b) 1000˚C, respectively. Strong cubic diffraction peaks, and no

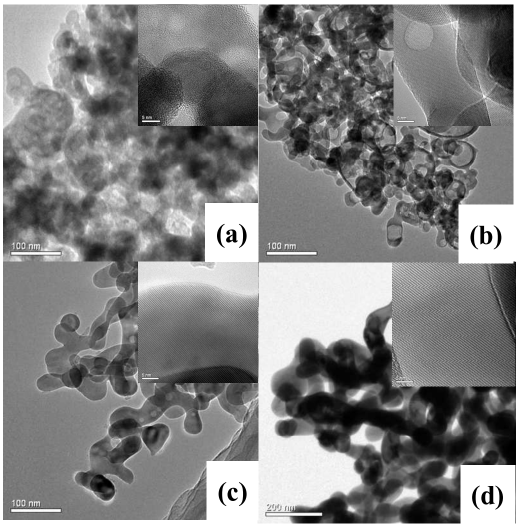


**Figure 4.** The TEM images of YAG in the different reaction conditions: (a) 800℃, (b) 900℃, (c) 1000℃, (d) 1100℃, respectively.

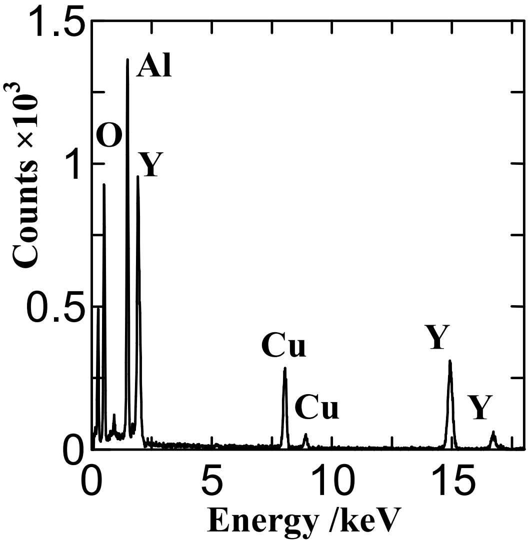


**Figure 5.** EDS analysis of the component phases of the rapidly solidified YAG eutectic.

obvious impurity peaks, can be observed for the powder prepared at this calcination temperature in the XRD pattern, as shown in Fig.3 (I) and (Ⅱ). The YAG and YIG powders synthesized by the AHC method showed much better sinter ability than those by the AC method.

**Powder morphology.** Fig. 4 shows the TEM images of the YAG powders produced by the AHC co-precipitation method, obtained at the conditions of (a) 800˚C, (b) 900˚C, (c) 1000˚C, and (d) 1100˚C for 2 h, respectively. The precursor is loosely agglomerated and the resultant YAG powders show good dispersity and excellent sinterability. From Fig. 4(a), the morphology of particles was found to be mono disperses and amorphous YAG with size range of 10–20 nm. Besides, the grain diameters are homogeneous and dispersibility is favorable. With the increase in of sintering temperature, the crystalline grain of YAG powders was enlarged and the crystallite shape was changed from irregular to regulation. From Fig. 4(d), it is observed that the crystal size of YAG powders is about 100 nm. However, prolonging calcination time and enhancing temperature will result in the aggregation of particles. Moreover, as shown by the high resolution TEM images in Fig. 4(c) and (d), the individual YAG crystallites appear to demonstrate a good crystallinity due to their clear lattice fringes. The molar ratio of samples analyzed by Energy-dispersive X-ray spectroscopy (EDS) is shown in Fig.5. The EDS patterns clearly indicated that, based on the Y, Al and O peaks [23], the final products were composed of YAG, and the Cu peaks corresponding to base plate. But the precursor powders prepared by AHC have a slight deviate from 60% to 64%, because of the gelatinous AlOOH formation.

## Conclusion

The Highly dispersed polycrystalline YAG and YIG powders have been prepared by co-precipitation technique in which $NH_4HCO_3$ or $(NH_4)_2CO_3$ is used as a precipitant. The XRD results indicated that the precipitant effects the preparation of pure-phase YAG or YIG powders. AC as precipitant could produce a hydroxide precursor, which transformed to a mixture at about 1300K. AHC as precipitant could produce a loosely agglomerated carbonate precursor. The resultant powders showed good dispersity and excellent sinterability.

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**Reference**

[1] T. Taira: Ceramic YAG lasers, C. R. Physique 8 (2007), P. 138

[2] A. ikesue, Y. L. Aung: Ceramic laser materials, Nature photonics. 2 (2008), P. 721

[3] J.Y. Pastor, J. LLorca, A. Martin, J.I. Pena, P.B. Oliete: Fracture toughness and strength of $Al_2O_3$–$Y_3Al_5O_{12}$ and $Al_2O_3$–$Y_3Al_5O_{12}$–$ZrO_2$ directionally solidified eutectic oxides up to 1900K, J. Eur. Ceram. Soc. 28 (2008), P. 2345

[4] F. Druon, F. Balembois, P. Georges: New laser crystals for the generation of ultrashort pulses, C. R. Phy. 8 (2007), P.153

[5] H. T. Yu, L.W. Zeng, C. Lua, W. B. Zhang and G. L. Xu: Synthesis of nanocrystalline yttrium iron garnet by low temperature solid state reaction. Mater. Charac., 62 (2011), P. 378

[6] M. Zeng, Y. J. Ma, Y. H. Wang, C. H. Pei: The effect of precipitant on co-precipitation synthesis of yttrium aluminum garnet powders, Ceram. Int., 38(8), (2012), P. 6951