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Preparation of $Y_3Al_5O_{12}$ Phosphor by Impinging Streams Homogeneous Precipitation-Molten Salt Assisted Method

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Fine and spherical $Y_3Al_5O_{12}$ (YAG) phosphor was synthesized by firing a preparative precursor with the molten salts of Na_2SO_4, S and K_2SO_4. The precursor was obtained by impinging streams homogeneous precipitation of yttrium and aluminum with ammonia water (AW) as precipitant. The experimental results show that the precursor transforms to YAG at about 700 ºC using molten-calcination method. Compared with the solid-state reaction method and impinging streams homogeneous precipitation-direct calcination method, the YAG phase transition temperature with the present method can be decreased about 800 and 200 ºC, respectively. The prepared YAG phosphor is of spherical structure with 200-300 nm by molten-calcination at 1000 ºC for 2 h and has better crystallinity and more regularly spherical morphology than that from direct-calcination method.

Key Words: YAG, Phosphor, Impinging streams homogeneous precipitation, Molten salt.

INTRODUCTION

Phosphor is often prepared by solid-state reaction technology. However, it requires high temperatures (>1500 ºC) to eliminate intermediate phases such as $Y_4Al_2O_9$ (YAM) and $YAlO_3$ (YAP)[1,2]. The phosphor prepared by this method has good quality of crystal and luminescence, but large particles size, broad particle distribution and impurity. Spherical phosphor with small particle size can improve its properties. Therefore, the wet chemical methods, such as co-precipitation, sol-gel and spray pyrolysis, are popular in preparing luminescent materials[3-5]. However, fine particles can easily grow together in the liquid and form aggregation. And the amorphous precursors require additional heat treatment at higher temperatures (> 1 000 ºC) to obtain well-crystallized product[6]. Therefore, hard aggregation is caused easily, which is not beneficial to the sintering of ceramic.

Impinging streams reactor, prepared through micromachining and precision machining technology, is a small response system. The streams impinge in the microchannel, resulting in an increased mass transfer for reaction and allowing for a decrease in the geometric size of the system[7]. The mixing characteristic size is between several microns and several hundred microns. Therefore, IS can provide intensified micromixing crucial to create a homogeneous environment for nucleation. Utilizing this advantage for preparing inorganic nanometer or the submicron materials with regular morphology is a brand-new field. It has been reported that TiO_2, ZnO, $Mg(OH)_2$, dyes and gold nanoparticles were synthesized by impinging streams reactors[8-13]. Molten salts can melt into ionic liquid at a relative low temperature and widely used as a chemical reaction medium to produce high temperature liquid surroundings for crystal growth[14,15]. In a solid-sate reaction, they modify growing surrounding and speed of crystal surface, which results in products with the special morphology and particle size.

In this paper, $Y_3Al_5O_{12}$ (YAG) phosphors were synthesized by the impinging streams co-precipitation-molten salt baking method. First, the YAG precursor was prepared using corresponding stoichiometric Y^{3+} and Al^{3+} with ammonia water as precipitant in a T-shaped impinging streams reactor. Then the as-prepared precursor was calcined with molten salts (Na_2SO_4 + S + K_2SO_4) into YAG phosphors at 700-1 000 ºC for 2 h, respectively. The powders were characterized by DSC-TG, FTIR, XRD and SEM. At the same time, calcination temperature and molten salts on the particle growth and morphology were also studied.

EXPERIMENTAL

The starting materials for YAG-based phosphor were rare earth oxide Y_2O_3 (99.99 %, Changsha, Hunan Non-Ferrous Metals Institute) and $Al(NO_3)_3·9H_2O$ (A.R., Tianjin Fine

Chemicals), K_2SO_4 (AR), Na_2SO_4 (AR), S (AR) and ammonia water (AR).

Y_2O_3 was dissolved in diluted nitric acid (HNO_3) and evaporated to remove the excess HNO_3. $Al(NO_3)_3 \cdot 9H_2O$ were dissolved in deionized water. PEG and $(NH_4)_2SO_4$ are both of analytical grade as the dispersant. The multi-cation solution was prepared according to stoichiometric proportion of $Y_3Al_5O_{12}$ and the total cation concentration was 0.22 M. The nitrate solution (reactant 1) was mixed in a container and then 1 wt % disperser (PEG400) and appropriately proportional $(NH_4)_2SO_4$ were added to the mixture with continuous stirring. Concentration of ammonium-water (reactant 2) was selected as 2.0 M.

General procedure: The reaction was operated in semibatch as shown in Fig. 1. 200 mL of the multi-cations solution (reactant 1) and 200 mL of the precipitant solution (reactant 2) were first drawn into the impinging streams reactor and then turned into the stirred tank reactor under strongly mechanical stirring at the same rate at 80 ºC. Resultant suspensions, after aging for 0.5 h at 80 ºC, were filtered, washed four times with deionized water, then with ethyl alcohol and dried at 100 ºC over 12 h and then the loose YAG precursors were obtained. The YAG precursors were directly calcined in air at 800, 900 and 1000 ºC for 2 h, respectively. On the other hand, the precursors mixed with molten salts (Na_2SO_4 + S + K_2SO_4) were calcined at 700, 800, 900 and 1000 ºC for 2 h, respectively. These sintered cakes were washed by deionized water and then dried to obtained objective phosphors.

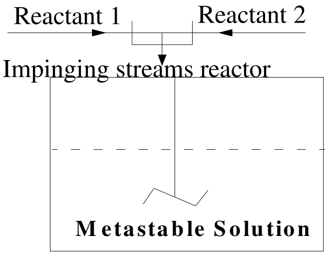

Fig. 1. Flow chart of impinging streams homogeneous precipitation

Detection methods: Thermal gravimetric and differential scanning calorimetry analysis (TG/DSC) of the precursors were made using a TG/DSC thermal analyzer with a heating rate of 10 ºC min^{-1}. FT-IR spectra were measured on an EQUINOX infrared spectrometer with KBr pellet technique. The phase identification was performed by using a conventional D/max X-ray diffractometer (XRD) with CuK$_\alpha$ radiation (λ = 0.15418 nm). The morphology and dispersion of the powder was taken with a JEOL JEM-5610LV scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Thermal analysis: Fig. 2 displays the TG/DSC curves of precursor powder with a heating rate of 10 ºC/min. DSC curve was consisted of two endothermic peaks and two exothermic peaks. The endothermic peak below 100 ºCcould be explained by the removal of physically adsorbed water and ethanol. The endothermic peak at 937.39 ºC could be due to decomposition of the precursors. The exothermic peak at 982.39 ºC could be attributed to crystallization and crystal growth of YAG. When the temperature was above 1000 ºC, there were no changes in TG and DSC curves which showed that the precursor powders were completely transformed to YAG cubic crystal phase. This was proved by the XRD results in Fig. 4(a). Major mass loss of the precursors occurred below 400 ºC. The overall weight loss was approximately 57.18 %.

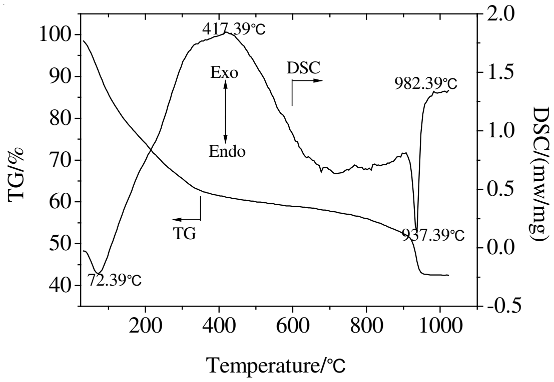

Fig. 2. DSC/TG traces of the precursors synthesized by impinging streams homogeneous precipitation

FT-IR spectra: FT-IR spectra of the powders produced by impinging streams homogeneous precipitation are shown in Fig. 3. The band near 3460 cm^{-1} was due to the stretching vibration of H_2O. The band about 1640 cm^{-1} was a result from the bending vibration of H_2O. The band about 1380 cm^{-1} was assigned to NO_3^- vibration. The peaks at about 791 and 692 cm^{-1} in Fig. 3 represent the characteristics Al-O metal-oxygen vibrations, while the peaks at about 723 and 555 cm^{-1} represent the characteristics Y-O metal-oxygen vibrations[16]. These characteristics metal-oxygen vibration absorption indicated formation of YAG structure.

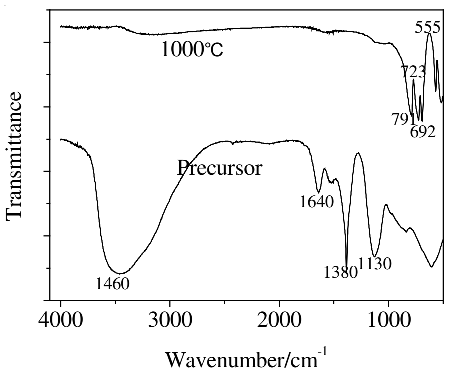

Fig. 3. FT-IR spectra of the powders synthesized by impinging streams homogeneous precipitation

Phase transition during calcination: XRD spectra of the powders synthesized by impinging streams homogeneous precipitation are given in Fig. 4. For YAG system, the directly synthesized particles in precipitation had amorphous phase. Post-treatment process at high temperatures is required for the crystallization of as-synthesized precursors. In the present work, the precursors were calcined by direct calcination method and calcination-molten salts of Na_2SO_4, S and K_2SO_4 assisted method. The powders calcined by direct calcination method were founded to be amorphous until 800 ºC (Fig. 4a).

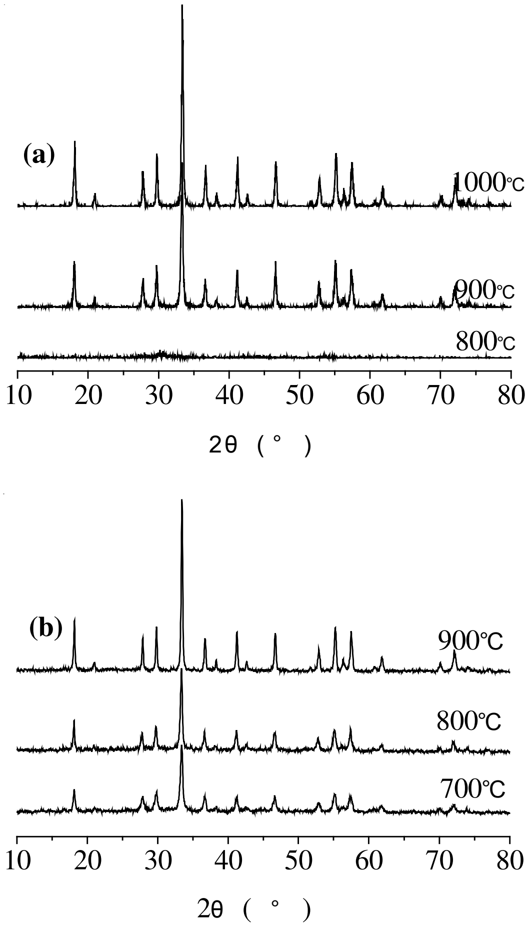

Fig. 4. XRD patterns of as-synthesized precursor powders calcined at different temperatures: (a) direct calcination method; (b) calcination-molten salt method

When the annealing temperature reached 900 ºC, the characteristic peaks of the cubic YAG phase appears, indicating that YAG phase mostly can be produced at temperature *ca.* 900 ºC. The diffraction pattern of the sample annealed at 900 ºC showed that all the peaks are due to the $Y_3Al_5O_{12}$ phase, which is in good agreement with JCPDS Card (No. 33-0040). It can be noticed from the spectra that intermediate phases [such as $Y_4Al_2O_9$ (YAM) and $YAlO_3$ (YAP)] and other impurities were not found, showing that YAG is the only crystalline component. When the annealing temperature was increased, the width of the diffraction peaks decreased and the intensity increased. This is an indication of the crystallization enhancement with increasing annealing temperature.

The precursors calcined by molten assisted method, crystallized as pure YAG at 700 ºC without the formation of intermediate phases. By comparing Fig. 4(a) with Fig. 4(b), phosphors with molten salts have a narrower diffraction peaks and high diffractive intensity than phosphors without molten salt. Compared with the solid-state reaction method and direct calcination method, the YAG phase transition temperature with the molten assisted method can be decreased about 800 and 200 ºC, respectively. This proves that molten salts can improve the crystallinity of YAG, because molten salts can provide a more stable and even temperature field.

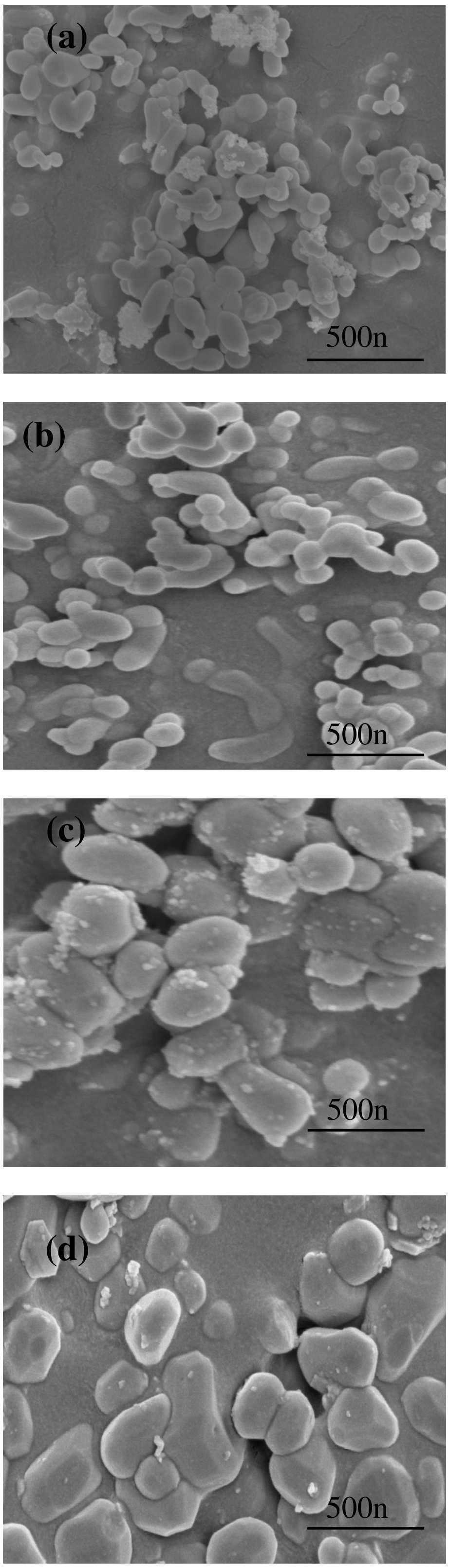

Fig. 5. SEM morphologies of as-synthesized precursor powders calcined by direct calcination method: (a) 1000 ºC and (b) 1200 ºC, by calcination-molten salt method: (c) 1000 ºC and (d) 1200 ºC

Phosphor morphology: Fig. 5 shows the SEM images of phosphors by direct calcination method and calcination-molten salt method at 1000 and 1200 ºC for 2 h, respectively. It is obvious that phosphor from calcination-molten salt method shows spherical morphology with particle size of 200-300 nm, while phosphor from direct calcination method shows quasi-spherical morphology with some agglomerate phenomenon.

This phenomenon proves that the transformation of morphology originates from the action of molten salts. That is to say, the (Na_2SO_4 + S + K_2SO_4) molten salts system has influence on the growth surroundings of crystal. At the same time, it is easy to find that the particle size of (c) and (d) is bigger than that of (a) and (b) because the molten salts can promote the growth of crystal.

Generally, the morphology of phosphor has close relationship with its growth surroundings[17,18]. The surroundings can be controlled through salt, temperature and time, *etc*. Molten salt can promote the reactants ions to move in liquid surroundings and form special morphology. When the temperature increases up to a certain extent, salts melt and liquid surrounding is formed, thus fastening transfer of reactants and speeding up the reaction. At the same time, owing to obstructing effect of molten salts, the resultants will not aggregate, so the fine and non-aggregate particle can be obtained.

Conclusion

$Y_3Al_5O_{12}$ (YAG) precursor was prepared by impinging streams homogeneous precipitation using ammonia water as precipitants. The as-synthesized precursor transformed to pure phase YAG without intermediate phases about 900 ºC by direct calcination method and quasi-spherical YAG phosphor was obtained by firing precursor at 1000 ºC for 2 h. Spherical and well dispersive YAG phosphor with particle size of 200-300 nm can be prepared by firing the mixture of precursor and complex molten salts (Na_2SO_4 + S + K_2SO_4) at 1000 ºC for 2 h. Pure phase YAG was obtained about 700 ºC by calcination-molten method. Compared with the solid state reaction method and direct calcination method, the YAG phase transition temperature with the molten assisted method could be decreased about 800 and 200 ºC, respectively.

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