Co-precipitation synthesis and luminescence behavior of Ce-doped yttrium aluminum garnet (YAG:Ce) phosphor: The effect of precipitant

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Abstract

YAG:Ce precursors were co-precipitated using ammonia water and ammonium hydrogen carbonate as precipitants, respectively. Phase transition of the precursors during sintering was compared between the two precipitants. The precursors synthesized with ammonia water transformed to YAG at about 1000 °C via YAlO3 phase. The precursors synthesized with ammonium hydrogen carbonate directly converted to pure YAG at about 900 °C. Comparing the powders produced with the two precipitants, the powders produced with ammonium hydrogen carbonate showed good dispersity. When sintered at 1600 °C, aggregation of the powders synthesized with the two precipitants both became severe. With increase the sintering temperature, the maximum wavelength of excitation and emission spectra of the phosphors synthesized with ammonium water hardly varied. While the maximum wavelength of excitation spectra of the phosphors synthesized with ammonium hydrogen carbonate unchanged, and the emission spectra showed red shift. Because of size effect and higher loss of cerium content, the emission intensity of phosphors prepared with ammonium hydrogen carbonate was lower than the phosphors prepared with ammonium water, when sintered at the same temperature.

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1. Introduction

Trivalent cerium activated yttrium aluminum garnet (YAG:Ce) has been found to be suitable for converting the blue light emitting diodes (LEDs) radiation into a very broad band yellow emission [1], which provides a basis to use YAG:Ce phosphor along with GaN LEDs to produce white light emitting diodes (WLEDs). Compared with traditional lighting, WLEDs have more advantage of high energy-efficiency, high reliability, long life, fast response and non-polluting. It is suggested that there would be a prosperous future in lamp market.

YAG-based phosphor was traditionally produced by solid-state reaction [2] between the component oxides which requires repeated mechanical mixing and extensive heat treatment to eliminate YAM (Y4Al2O9) and YAP (YAlO3) [3] intermediate phases, which deteriorates the luminescent properties. Co-precipitation method, because of its apparent advantage of fine homogeneity, high reactivity of starting materials and lower sintering temperature, is a novel route to synthesize fine phosphor [4]. Previous work studied preparation YAG-based phosphor by different precipitants, such as ammonia water [5,6], ammonium hydrogen carbonate [7], oxalate [8], urea [9]. Comparing these precipitants, solubility of oxalate was low and pH of the precipitation process must be strictly controlled for complete precipitation of aluminum cation. When using urea as precipitant, solution must be heated at high temperature for release of OH− and CO32−. High temperature and slow release of OH− and CO32− was disadvantageous to prepare nanometer and good dispersible powders. Therefore, ammonia water and ammonium hydrogen carbonate were more suitable precipitants to co-precipitate powders.

Chemical composition as well as physical properties of the precursors have dramatic effect on luminescent properties of the phosphors. Previous work showed that ammonium hydrogen carbonate (AHC) exceeds ammonia water (AW) for the production of less-agglomerated, well-sinterable powders [10] via precipitation.

In this work, Ce-doped YAG phosphor precursors were synthesized by different precipitants including AW and AHC. Phase evolution of the precursors, morphologies and the luminescent
properties of the phosphors as a function of sintering temperature were compared.

2. Experimental

2.1. Materials

The starting materials for YAG-based phosphor were rare earth oxide Y$_2$O$_3$ (99.99%, Shanghai Yuelong Non-Ferrous Metals Limited), Ce(NO$_3$)$_3$·6H$_2$O (A.R., Sinopharm Chemical Reagent Co., Ltd.) and Al(NO$_3$)$_3$·9H$_2$O (A.R., Sinopharm Chemical Reagent Co., Ltd.).

Y$_2$O$_3$ was dissolved in dilute HNO$_3$ and evaporated to remove the surplus HNO$_3$. Ce(NO$_3$)$_3$·6H$_2$O and Al(NO$_3$)$_3$·9H$_2$O were dissolved in deionized water. The multi-cation solution was prepared according to stoichiometric proportion of Y$_{2.95}$Ce$_{0.05}$Al$_5$O$_{12}$ and the total cation concentration was 0.24 M. Concentration of AW was selected as 3 M. For comparison, AHC of 1.5 M was also made by dissolving AHC into deionized water.

2.2. Powder synthesis

For multi-cation precipitation, the reverse-strike technique (adding multi-cation solution to the precipitant solution) has the advantage of higher cation homogeneity in the precursors [11] and was used in this study. Precursors were produced by dropping 250 ml of the multi-cation solution at a speed of 1.5 ml/min into 250 ml of the precipitant solution under magnetic stirring at room temperature. It was stirred for another 30 min after finish dropping. Resultant suspensions, after aging for 8 h at 50°C, were filtered, washed four times with deionized water, rinsed with ethyl alcohol and dried at 120°C over 12 h. By finely milled in an agate mortar, the precursors were preheated for 2 h at 500°C in air. After an intermediate grinding, the precursors were additionally sintered at different temperatures for 2 h in a weakly reducing atmosphere consisting of a nitrogen–hydrogen mixture containing 8% volume of hydrogen.

2.3. Powder characterization

The composition of precursors was assayed by an IRIS Advantage 1000 inductively coupled plasma atomic emission spectrometer (ICP-AES).

Phase identification was performed on a Rigaku D/Max X-ray diffractometer (XRD) using nickel filtered Cu K$_\alpha$ radiation with a scanning speed of 6° min$^{-1}$. FT-IR spectra were measured on an EQUINOX Infrared Spectrometer with KBr pellet technique.

Differential scanning calorimetry (DSC) of the original precursors were made on a DSC analyzer (Model C404/6/7, NETZSCH-Gerätebau, Selb, Germany) in flowing nitrogen atmosphere with a heating rate of 10°C/min. Thermal gravimetric analyses (TG) of the original precursors were made on a TG analyzer (Mode TGA 1000, USA) in flowing nitrogen with a heating rate of 10°C/min.

Powder morphologies were observed by field emission scanning electron microscopy (FESEM, Model FEI—Sirion 200, Philips, The Netherlands). Samples were ultrasonically dispersed into acetone, and the suspension was spread on the surface of copper plate. All samples were coated with a thin layer of aurum for conductivity before observation.

The excitation and emission spectra were obtained on a LS 50B luminescence spectrometer. Measurement was performed at room temperature.

3. Results and discussion

3.1. Cation contents in the precursor

Table 1 shows the type loss of cations in the precursors and the variation of pH. The initial pH is the pH of precipitant solution and the final pH is the pH of solution after precipitation.

<table>
<thead>
<tr>
<th>Precipitant</th>
<th>Loss of cation (at%)</th>
<th>Initial pH</th>
<th>Final pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>AW</td>
<td>3.36 × 10$^{-6}$</td>
<td>9.42 × 10$^{-4}$</td>
<td>9.52 × 10$^{-5}$</td>
</tr>
<tr>
<td>AHC</td>
<td>1.39 × 10$^{-3}$</td>
<td>4.30 × 10$^{-4}$</td>
<td>8.66 × 10$^{-3}$</td>
</tr>
</tbody>
</table>

3.2. Phase transition during sintering

XRD spectra of the powders produced by AW and AHC are shown in Fig. 1. The powders produced by the two precipitants were found to be amorphous until 800°C. From 900°C, different phase development was observed. For the powders produced by the AW (Fig. 1a), hexagonal YAlO$_3$ crystallized at 900°C with the presence of peaks of YAG. At 1000°C, the hexagonal YAlO$_3$ phase disappeared and YAG was the only phase.

The precursors produced by the AHC, crystallized as pure YAG at 900°C without the formation of intermediate phases.

![Fig. 1. XRD spectra of the powders synthesized with AW (a) and AHC (b).](http://www.paper.edu.cn)
Above 900 °C, continued refinement of peak shapes and intensities were observed.

The precursors produced by the AHC directly converted to pure YAG at about 900 °C, which indicated higher cation homogeneity of the precursors produced by AHC. Refinement of peak shapes and intensities indicated crystallite growth of the powders as temperature increase.

3.3. FT-IR spectra

FT-IR spectra of the powders produced with AW and AHC are shown in Fig. 2. The band near 3500 cm\(^{-1}\) was due to the stretching vibration of H\(_2\)O. The band about 1630 cm\(^{-1}\) was a result from the bending vibration of H\(_2\)O. The band about 1400 cm\(^{-1}\) was assigned to NO\(_3^-\) vibration. In Fig. 2b, the bands around 1450 and 860 cm\(^{-1}\) are due to CO\(_3^{2-}\) vibrations. These bands became weaker, when the powders were heated to higher temperature.

The peaks at about 790 and 684 cm\(^{-1}\) in Fig. 2a represent the characteristics Al–O metal–oxygen vibrations [11], while the peaks at about 720 and 565 cm\(^{-1}\) represent the characteristics Y–O metal–oxygen vibrations [12]. Similarly, the peaks at about 788, 692, 723 and 567 cm\(^{-1}\) in Fig. 2b represent the characteristics metal–oxygen (Y–O and Al–O) vibrations. These characteristics metal–oxygen vibration absorption denoted formation of YAG structure.

3.4. Thermal analysis

DSC/TG traces of the precursors produced with AW are given in Fig. 3a. The broad endothermic peak at about 160 °C was due to the removal of water. The sharp exothermal peak at 921 °C was caused by the crystallization of YAP, as evidenced by the XRD results in Fig. 1a. The exothermic peak at about 1015 °C corresponds to YAP reacting with Al\(_2\)O\(_3\) to form YAG [3]. The TG curve showed complete decomposition of the precursors achieved at about 850 °C with a total weight loss of 38.74%.

DSC/TG traces of the precursors produced with AHC are given in Fig. 3b. The exothermic peak around 935 °C was assigned to the crystallization of YAG, which is evidenced by the XRD results in Fig. 1b. Major mass loss of the precursors occurred below 600 °C. The total weight loss is 50.48%.

3.5. Phosphor morphology

Fig. 4a–c shows SEM morphologies of the powders produced with AW sintered at different temperatures. In Fig. 4a and b, the large particles may be composed of primary nano-sized particles, which were bridged by hydrogen bond and the huge capillary force generated during drying. The powders sintered below 1600 °C remained the similar sizes distribution and aggregation. Sintered at 1600 °C, particles merged and sharply grown. Aggregation became much severer.
Fig. 4. FSEM morphologies of the powders synthesized with AW: sintered at 800 °C (a), 1200 °C (b) and 1600 °C (c), with AHC: sintered at 800 °C (d), 1200 °C (e) and 1600 °C (f).

Fig. 4d–f shows the powders produced with AHC. When powders sintered below 1600 °C, particles showed much better dispersity. After sintered at 1600 °C, particles rapidly grown. Compared with powders produced with AW, aggregation of powders produced with AHC was little weaker.

Comparing the powders produced by the two precipitant, particle size distribution of the powders produced with AW was wider than the powders produced with AHC, which was likely to result from the more greater variation of pH when using AW as precipitant. The powders produced by AHC showed even better dispersity, which result from different chemical composition of the precursors. The precursors produced by AW were bridged by hydrogen bond. Though washed with ethyl alcohol and decreased the extent of agglomeration, the precursors were still strongly agglomerated. For the precursors produced by AWC, however, possibility of hydrogen bond formation was reduced and the water was more easily removed. Furthermore, escape of CO₂ during sintering also released the aggregation.

3.6. Luminescence properties of YAG:Ce synthesized with different precipitants

Excitation and emission spectra of phosphors synthesized with AW and AHC sintered at different temperature are shown in Figs. 5 and 6, respectively. These excitation bands were due to the electron transition from ground state of Ce³⁺ (2F⁵/₂, 2F⁷/₂) [13] to the different crystal field splitting components of excited 5d state. The emission of Ce³⁺ is ascribed to the electron transi-
tions from the lowest crystal-splitting component of 5d level to the ground state Ce$^{3+} \left( ^2F_{5/2}, ^2F_{7/2} \right)$.

Following the increase of temperature, excitation and emission intensity increased. The increase of intensity resulted from enhancement of crystallization degree and the decrease of surface defects [14]. Despite using different precipitant and sintered at different temperature, the maximum excitation wavelength hardly changed.

The emission spectra of phosphors synthesized by different precipitants were compared. Although sizes distribution of phosphors synthesized with AHC was more uniform and aggregation was much weaker, the emission intensity of phosphors synthesized with AHC was lower than with AW, when sintered at the same temperature. According to cation contents and morphologies analysis, the specific area of phosphors produced with AHC was larger and the loss of Ce using AHC was higher than using AW. Large specific area brought on more surface defects, which lead to more possibility of nonradiative recombination. The high loss of Ce activator also led to decrease in emission intensity.

With the increase of sintering temperature, the maximum emission wavelength of phosphors synthesized with AW nearly unchanged. While the maximum emission wavelength of phosphors synthesized with AHC showed red shift. From the observation of morphologies, the phosphors synthesized by AHC had nano-sized particles. Nano-sized particles usually showed blue shift of the emission spectra [15]. Following the temperature increase, the particles grown and blue shift phenomena disappeared. Therefore, red shift was observed when sintering temperature increased.

4. Conclusions

YAG:Ce precursors were co-precipitated using ammonia water and ammonium hydrogen carbonate as precipitants, respectively. The powders synthesized by ammonium hydrogen carbonate showed much better dispersity, despite of higher loss of cation contents. Phase evolution of the precursors during sintering was compared between the two precipitants. The precursors synthesized with ammonia water transformed to YAG at about 1000°C via YAlO$_3$ phase. The precursors synthesized with ammonium hydrogen carbonate directly converted to pure YAG at about 900°C.

When the phosphors using ammonium water sintered at different temperature, the maximum wavelength of excitation and emission spectra hardly varied. As the phosphors using ammonium hydrogen carbonate sintered at different temperature, the maximum excitation wavelength unchanged, and the emission spectra showed red shift. Because phosphors prepared with ammonium hydrogen carbonate owned large specific area and high loss of Ce activator, the emission intensity of the phosphors was lower than the phosphors prepared with ammonium water, when sintered at the same temperature.

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