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Synthesis of single-phase nanocrystalline garnet phosphor derived from gel-network-coprecipitation

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Three compounds exist in the system Y_2O_3-Al_2O_3: $Y_4Al_2O_9$, $YAlO_3$, and $Y_3Al_5O_{12}$ [1]. $Y_3Al_5O_{12}$(YAG), and the most important of these compositions exists in the cubic form with a garnet structure. It is an important crystal for fluorescent and solid-state lasers, because it exhibits a thermally stable lattice, a well-determined crystal structure, and most importantly, resists saturation at high current excitation [2, 3]. Single crystals of Cr^{3+}-doped YAG for example, are used in solid state lasers and Tb^{3+}-doped YAG gives a characteristic narrow-band phosphor suitable for contrast-enhanced display applications [4, 5].

YAG phosphor powders are normally synthesized at relatively high temperatures by solid-state reaction between Y_2O_3 and Al_2O_3. Such conditions lead normally to powders of relatively large and varied grain sizes (5–20 μm) and varying impurity content. There are often problems in obtaining phase-pure material because of the intermediate formation of other phases, such as $Y_4Al_2O_9$ and $YAlO_3$ [6]. To achieve the desired phase purity and required particle size, high temperature treatment (>1600 °C) and extensive ball milling, which generally introduces additional impurities and defects and greatly reduces luminescence efficiency, are essential. For phosphor applications, it is desirable to have a fine particle size for high resolution and chemical purity for optimum chromaticity and brightness [7]. A few chemical synthesis techniques, such as sol-gel [8, 9], precipitation of hydroxides [10, 11], thermal decomposition of nitrates [12], hydrothermal treatment [13] and combustion synthesis [14], have also been used to prepare YAG powders. The literature concerning phase formation in these powders, however, contains conflicting results.

In this study, a novel low temperature synthesis technique for nanocrystalline garnet phosphors using a gel-network-coprecipitation method is reported. The samples prepared in this work were designed to have an overall composition $Y_{3-0.2-x}Al_5O_{12}$:$Eu_{0.2}$, Bi_x ($x = 0$ or 0.002). Y_2O_3 and Eu_2O_3 (99.99% pure, Shanghai Yuelong New Materials Co., Ltd.), $Al(NO_3)_3 \cdot 9H_2O$, $NH_3 \cdot H_2O$ and $Bi(NO_3)_3 \cdot 5H_2O$ (analytical grade, Beijing Shuanghuan Weiye Reagent Co., Ltd.), and gelatin (chemical purity Cangzhou Jinjian gelatin Co., Ltd.) were used as starting materials. Aqueous nitrate solutions of rare earth ions were prepared by dissolving high-purity Y_2O_3 and Eu_2O_3 in HNO_3 then diluting with deionized water. 25 cm^3 of 0.2 $mol \cdot dm^{-3}$ aluminum nitrate solution was mixed uniformly with 14 cm^3 of 0.2 $mol \cdot dm^{-3}$ yttrium nitrate and 2 cm^3 of 0.1 $mol \cdot dm^{-3}$ europium nitrate solution in a beaker under stirring. Then 6 g gelatin was dissolved in the mixed nitrate solution with vigorous stirring at 80 °C and continuously stirred for 2 h at about 80 °C. Then the mixture was cooled to 4 °C, turning to a yellowish gel. The gel was cut into small pieces and then soaked in 75 cm^3 of 1:1 $NH_3 \cdot H_2O$ solution for 24 h at 4 °C. The hydroxides were precipitated in the gel-network. The gel was washed with cooled distilled water to remove nitrate ions and residual ammonia and then dried under vacuum at 110 °C. The dried gel obtained is termed the

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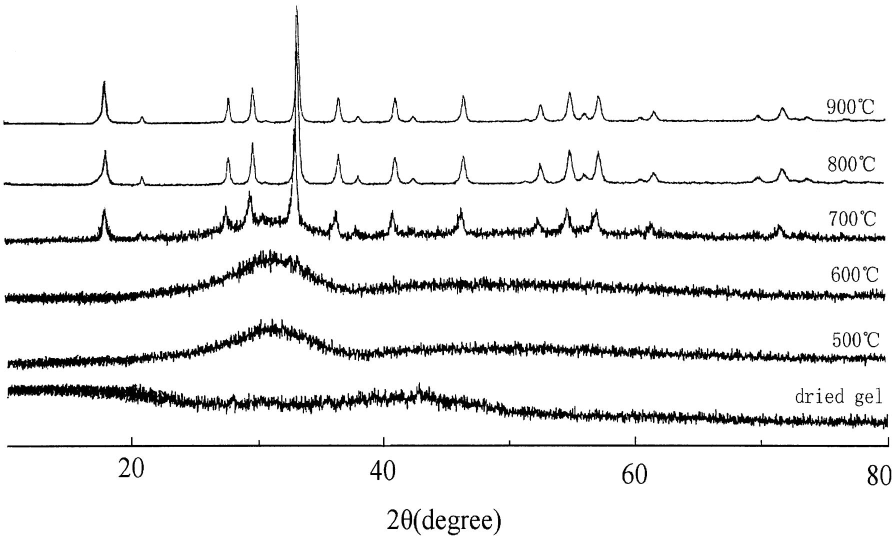

Figure 1 XRD patterns of the $Y_{2.8}Al_5O_{12}:Eu_{0.2}$ precursor calcined at difference temperature.

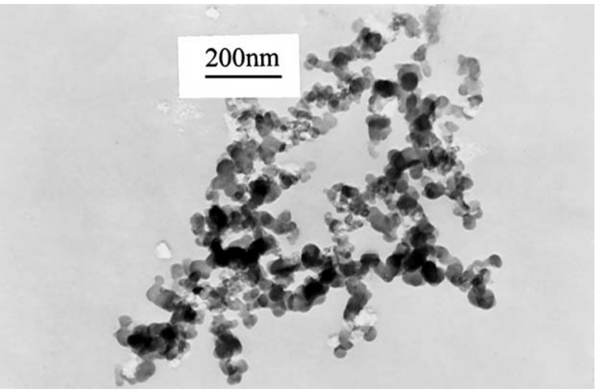

Figure 2 TEM micrographs of the YAG:Eu powders calcined at 900 °C.

"precursor". The precursor was preheated at 400 °C for 2 h in air. After an intermediate grinding, the powder was subsequently fired at various temperatures from 500 to 900 °C for 3 h in a muffle furnace in air, producing fine phosphor powders.

X-ray diffraction analysis (XRD) of the product was recorded using a Bruker D8 Advance X-ray diffractometer (Cu K_α radiation). The particle size and morphology of the heat-treated powders were examined using a 200 CX transmission electron microscope (TEM, Model 200CX, Jeol, Tokyo, Japan). The photoluminescence spectra of phosphors were measured at room temperature on a Hitachi-850 fluorescence spectrophotometer.

X-ray patterns for the decomposition products of the precursor after using different calcination temperatures are shown in Fig. 1. The precursor remained amorphous (to X-rays) up to 600 °C. At 700 °C, weak characteristic peaks of YAG phase appeared, indicating the beginning of crystallization of the pure garnet phase. Further heating of the precursor up to 900 °C showed no change in phase composition, but there was an increase in the intensity of the peaks. XRD indicates that YAG is the only crystalline phase to form during calcination. It can be concluded that YAG appears to

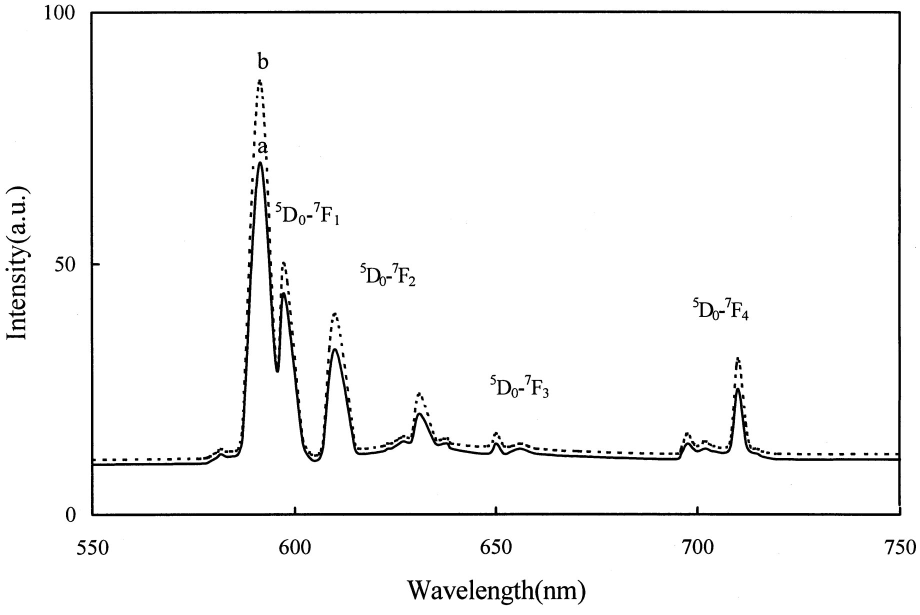

Figure 3 Emission spectra of (a) YAG:Eu and (b) YAG:Eu,Bi ($\lambda_{ex} = 396$ nm).

crystallize directly from the amorphous precursor without the formation of any intermediate phase, indicating the high cation homogeneity of the precursor. No difference could be observed between the XRD patterns of YAG:Eu,Bi and YAG (JCPDS No. 33–40), indicating that some of the Y^{3+} ion sites have been occupied by Eu^{3+} and Bi^{3+} ion in YAG:Eu,Bi crystallites. Thus, phase-pure YAG phosphor can be synthesized by a gel-network-coprecipitation method at a low crystallization temperature.

A TEM image showing the morphology and the size distribution of YAG:Eu phosphor calcined at 900 °C is shown in Fig. 2. The sample of the as-prepared YAG:Eu phosphor is uniform with well-distributed spherical or elliptical particles with a size range from 40 to 50 nm. This is consistent with estimated particle size (37–43 nm) from the XRD peak broadening. The TEM image of YAG:Eu,Bi was similar to the YAG:Eu, the present of a small Bi^{3+} concentration in the YAG:Eu phosphor had no influence on particle size. Therefore, the as-prepared phosphor does not need to be reground before it is applied.

The photoluminescence (PL) spectrum of $Y_{2.8}Al_5O_{12}:Eu_{0.2}$ phosphor nanocrystallites calcined at 900 °C for 3 h is illustrated in Fig. 3. The emission of the YAG:Eu phosphor is mainly from $^5D_0$ with the hypersensitive transition $^5D_0 \rightarrow {}^7F_1$ as the most prominent group at about 590 nm which derives from the magnetic dipole transition [15], indicating that the Eu^{3+} ions occupy centrosymmetrical sites. The spectrum also shows many additional weak lines due to the spin-orbit split ground states ^7F_J ($J = 2, 3, 4$) (Fig. 3a), each of which is further split by the crystal field. The character of the spectrum clearly indicates that the phase containing Eu^{3+} has the yttrium aluminum garnet crystal structure (C_2 symmetry), and that some of the Y^{3+} ion sites have been occupied by Eu^{3+} ions in YAG:Eu. The introduction of a small Bi^{3+} concentration ($x = 0.002$) in the YAG:Eu phosphor results in the enhancement of Eu^{3+} emission (Fig. 3b), pointing to the presence of an energy transfer from the Bi^{3+} to Eu^{3+}, indicating that Eu^{3+} emission can be sensitized by Bi^{3+}.

Acknowledgments

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