

YAG:Ce³⁺ Nanophosphor Synthesized with the Salted Sol-Gel Method

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ABSTRACT

Nano-phosphors of Y₃Al₅O₁₂:Ce³⁺ (YAG:Ce) were synthesized with a novel salted sol-gel method, in which aqueous solution of inorganic salts (yttrium/cerium nitrates) were used along with the metal alkoxide precursor, aluminum sec-butoxide, Al(OC₄H₉)₃. YAG single phase was formed at temperature as low as 800 °C. Luminescence of YAG:Ce reached the maximum intensity when calcined above 1350 °C. The SEM image reveals that the grain sizes of the nano-phosphors calcined at 1100 °C are in a range of 50-150 nm.

Keywords: photoluminescence, nano-phosphor, YAG:Ce, sol-gel

1 INTRODUCTION

Nano-phosphors have drawn considerable attentions in recent years.^{1,2} Such ultra-fine powders of phosphors have strong potential to improve fineness of luminescent display images, energy efficiency of luminescent lamps and LED-phosphor white light sources because of reduction of internal light scattering. Before the eighties of the last century, however, it was found that the luminescence efficiency of phosphors was seriously degraded when grain size smaller than 1 mm. This was ascribed to the affect of surface defects.³ Ratio of surface area to volume of grains increases with reduction of grain size, and surface influence becomes more serious. In the nineties, it has been reported that efficient luminescence can

be still observed in nano-powders of luminescent materials,^{2,4} if the crystallinity is good. For the phosphors fabricated with traditional solid-state chemical reaction, powders with small size have to be synthesized at lower calcining temperatures and short calcining time. This results in poor crystallinity. In opposite, the luminescent efficiency could remain high if the quality of the crystallinity of nano-phosphors is guaranteed. On the other hand, for the applications of display panels and lighting industries, a large amount of phosphors is needed. Unfortunately, most technologies currently used to fabricate nano-structured phosphors, for example, various precipitation methods, are not so efficient for mass production.

We have recently developed a novel modified sol-gel method, called salted sol-gel (SSG) method,⁵ to prepare nano-powders. The conventional sol-gel technique has been used to produce nano-structured materials, such as thin film coating and nano-powders. But, as precipitation method, the method is still limited for producing a large amount of powders. That is because many metallic alkoxides are solid and their solubility in organic solvents is not high. For example, commercial yttrium isopropanol is a solution with a concentration of 10 grams of it in 100 ml isopropanol. In SSG method, one of compositions of phosphors is liquid alkoxide, the others are aqueous solution of their salts. SSG is a kind of wet chemical methods and provide a way to prepare uniform chemical mixture at almost atomic level. It is expected to produce nano-phosphors in an economic way and with good crystallinity.

In this work, $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG):Ce³⁺ is selected as an example. YAG:Ce is the unique phosphor currently used in LED-phosphor white light sources.⁶ Part of blue emission of LEDs at 460 nm is down-converted into broad band yellow emission centered at 550 nm through the phosphor. The commercial products are made by solid-state chemical reaction with grain size greater than 1 μm . With the help of flux, the firing temperature is in the range of 1400–1600 °C. Our work demonstrates that ultra fine powders of YAG:Ce in nano-scale can be synthesized with the salted sol-gel method at much reduced calcining temperatures. The nano-phosphor shows efficient luminescence comparable with that of the commercial product.

2 EXPERIMENTAL

Nano-phosphors of $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (YAG:Ce) were synthesized with the salted sol-gel (SSG) method. Yttrium and cerium nitrate (or acetate) salts were dissolved in hot water (60 °C) in order to limit the amount of water to be used. The solution was stirred for uniformity. Liquid aluminum sec-butoxide (ASB) was diluted in a liquid mixture of isopropanol and n-Heptane or directly used without dilution. The nitrate solution was quickly blended into ASB with rapid stirring. White cloudy colloidal suspensions immediately appeared. The hydrolysis reaction of ASB with water is an exothermic process. Butyl alcohol is released and smelt in the multiple steps of hydrolysis. The isopropanol and n-heptane used in the nitrate solution may slow down the speed of hydrolysis and polymerization processes.

Al_2O_3 forms nano-cluster-network of nanopores with sizes of about 2 nm - 5 nm. Yttrium nitrate clusters are entrapped in these nano-pores. In order to avoid re-dissolving of the nitrate clusters, water used in the solution is kept as less as possible. After 10 minutes or so, transparent wet gels were obtained. The gels were baked at 90 °C for a day. They then became transparent dry gels. The dry gels can be easily ground into fine powders. The powders were heated at 600 °C

for 2 hours to decompose $\text{Y}(\text{NO}_3)_3$ and to remove any organic residuals. The sample is now a mixture of nano-clusters of Al_2O_3 with nanopores in which nano-clusters of Y_2O_3 were embedded.

The powder samples were fired at elevated temperatures from 700 °C to 1450 °C for two-three hours in air or slightly reducing atmosphere for XRD, SEM and luminescence measurements. X-ray diffraction was done using a Rigaku X-ray diffractometer. For Photoluminescence and excitation spectra a SPEX FluoroMax2 spectrophotometer was employed.

3 RESULTS AND DISCUSSION

3.1 X-ray diffraction (XRD)

Figure 1 shows the XRD pattern of YAG:Ce calcined at 800 °C for two hours in air. Figure 2 presents the dependence of relative intensity of XRD peak ($2\theta = 32.3^\circ$) on calcination temperatures. All the samples were calcined for three hours. For comparison, XRD data, taken from K. Ohno and T. Abe,⁷ of YAG prepared by solid state chemical reaction with and without flux (BaF_2) are also shown. It can be seen that, without flux, no YAG phase is formed below

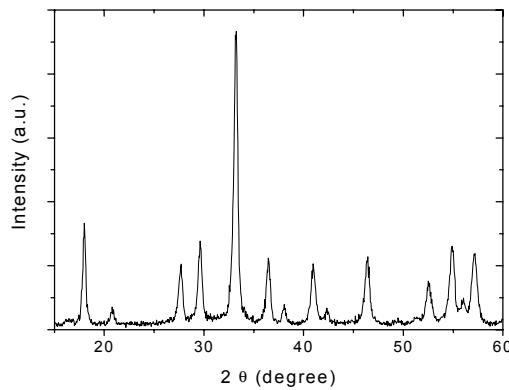


Fig. 1. XRD spectrum of YAG:Ce sintered at 800 °C for two hours in air.

1300 °C. At 1600 °C, the diffraction intensity does not reach the potential maximum. Even with flux, the highest crystallinity appears at 1500 °C. Below 1200 °C, the crystallinity is only 5%. In

contrast, YAG phase by SSG method is well formed at 800 °C as shown in Fig. 1. Above 1350 °C, the maximum crystallinity is obtained. This can be understood. Since the uniformity of the mixture of Al₂O₃ and Y₂O₃ by SSG is at a level of nano-scale or almost atomic level. The diffusion length for complete reaction is only 1/1000 of that of solid-state chemical reaction.

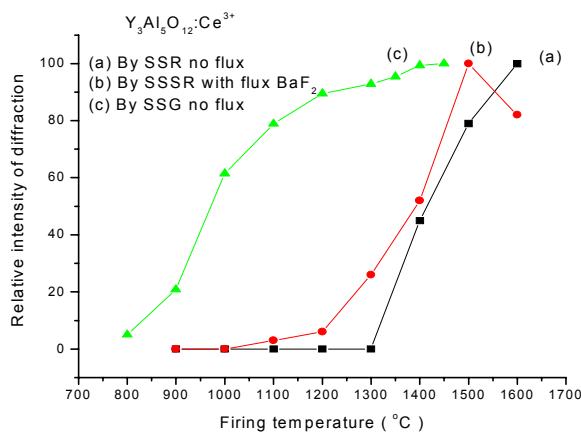


Fig. 2. Dependence of the relative intensity of XRD on calcining temperatures.

3.2 SEM image

SEM image of YAG:Ce powders calcined at 1100 °C in air is given in figure 3. It can be seen that the YAG particles are aggregated. The

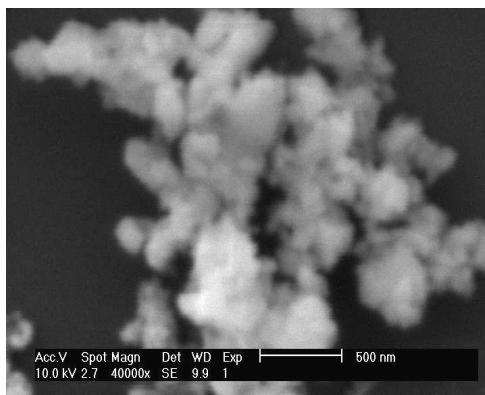


Fig. 3. SEM image of YAG sample produced with SSG method sintered at 1100 °C.

particle sizes are in a range of 50-150 nm. Aggregation is the natural process in preparation of nano-phosphors by SSG method because no

special dispersion agent is employed. In fact, isopropanol and n-heptane used in the synthesis process play a role of dispersion of nano-clusters, but they are burnt out in the heating processes. However, for the applications to lighting or displays, in preparation of slurry of phosphors with certain liquids such as aqueous polyvinyl alcohol solution, the aggregated particles can be separated and dispersed (a minor grinding may be used).

3.3 Photoluminescence

Typical photoluminescence and excitation spectra of YAG:1.5%Ce are shown in figure 4. The sample was calcined at 1350 °C for 3 hours in the N₂ + 5% H₂ flow. The emission band is at 534 nm with a broad shoulder near 580 nm. The most intensive excitation peak is located at 460 nm, which is well matching to the blue emission of LEDs.

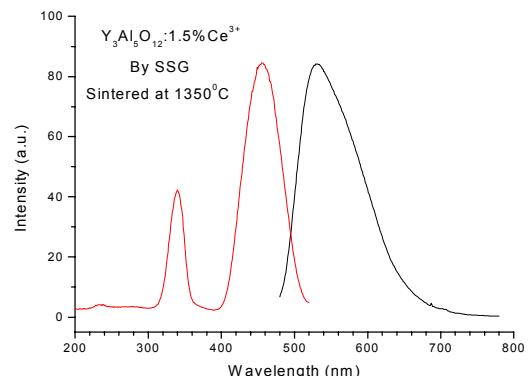


Fig. 4. Emission and excitation spectra of YAG: 1.5%Ce, calcined at 1350 °C for 3 hours.

Figure 5 shows the dependence of luminescence intensity of YAG: 1.5%Ce by SSG on calcination temperatures. It can be seen that the sample shows the maximum intensity if calcined above 1350 °C. For comparison, luminescence data, taken from K. Ohno and T. Abe, of YAG:Tb, are shown in the figure. The general features are similar to the case of XRD. The intensity of luminescence of YAG:Tb sintered at 1600 °C by SSR without flux is still much below the maximum intensity of that by

SSR-flux (Fig.5). With flux, the sample reaches the maximum intensity when sintered at 1500 °C. In contrast, the sample by SSG method reaches the maximum intensity when calcined above 1350 °C.

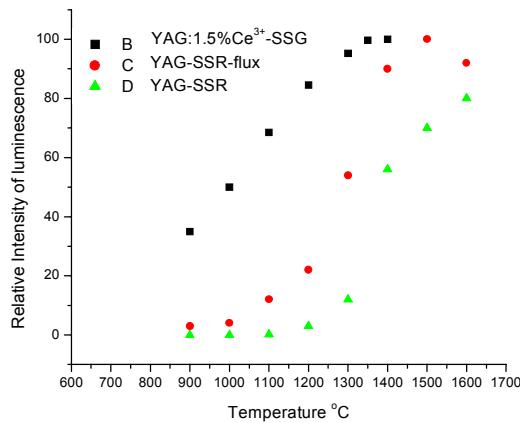


Fig. 5. Dependence of luminescence intensity of YAG:1.5%Ce on calcining temperatures.

Concentration dependence of the luminescence intensity of YAG:Ce³⁺ were also measured. With cerium concentration of 0.5% to 3%, samples show almost the same luminescence intensity, indicating that concentration quenching start to appear when the concentration greater than 0.5%. Because of concentration quenching, the luminescence intensity does not increase linearly with increasing the concentration. In addition, the emission wavelength was found to shift to the longer wavelength side as increasing Ce³⁺ concentration.

4 CONCLUSION

X-ray and luminescence results reported here demonstrate that the salted sol-gel method is a useful technology to fabricate nano-phosphors. Uniform mixture of chemical compositions at nano-scale or almost atomic level ensures a good crystallinity at lower calcining temperatures and short calcining period. These provide basic synthesis conditions to obtain phosphors with grain size of tens or hundreds of nano-meters. Such ultra fine phosphors may improve emissive

displays and energy efficiency of luminescence lighting sources.

5 ACKNOWLEDGEMENT

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