PHOSPHOR SYNTHESIS ROUTES AND THEIR EFFECT ON THE PERFORMANCE OF GARNET PHOSPHORS AT LOW-VOLTAGES

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ABSTRACT

Garnet phosphors have potential for use in field emission displays (FEDs). Green-emitting $\text{Gd}_3\text{Ga}_5\text{O}_{12}:\text{Tb}$ (GGG:Tb) and $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Tb}$ (YAG:Tb) are possible alternatives to $\text{ZnO}:\text{Zn}$, because of their excellent resistance to burn, low-voltage efficiency, (3.5 lm/W from GGG:Tb at 800 V), and saturation resistance at high power densities. Hydrothermal and combustion synthesis techniques were employed to improve the low-voltage efficiency of YAG:Tb, and $\text{Y}_3\text{Ga}_5\text{O}_{12}:\text{Tb}$ (YGG:Tb). Synthetic technique did not affect low-voltage (100-1000 V) efficiency, but affected the particle size, morphology, and burn resistance. The small particle size phosphors obtained via hydrothermal (<1 μm) and combustion reactions (<1 μm) would benefit projection TV, high-definition TV (HDTV), and heads-up displays (HUDs), where smaller pixel sizes are required for high resolution.

INTRODUCTION

Field emission displays (FEDs) require phosphors that are highly efficient at low voltages (<1 kV). To compete with liquid crystal displays (LCDs) in terms of power consumption, the red, green, and blue phosphor compositions in an FED must have efficiencies of 4, 6, and 1 lumens/watt (lm/W) respectively [1]. Phosphors under consideration for use in FEDs include $\text{Y}_2\text{O}_2\text{S}:\text{Eu}$ (red), $\text{ZnS}:\text{Cu},\text{Al}$ (green), and $\text{ZnS}:\text{Ag},\text{Cl}$ (blue). Oxide phosphors are preferred in these devices since sulfides are known to contaminate the emitter tips by the release of corrosive, sulfur-related gases (e.g., SO_2 , SO) under prolonged electron bombardment [2]. Unfortunately, the cathodoluminescence efficiencies of oxides at low voltages are usually lower than those of sulfides. The cathode-to-screen distance in FEDs is much shorter than in a conventional cathode-ray tube (CRT), and the phosphor is exposed to higher current densities due to low voltage operation. Therefore, in addition to low-voltage efficiency, other major requirements for FED phosphors include resistance to saturation and Coulombic aging at high current densities. Garnet host lattices such as $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) are known to resist degradation caused by high power density, and exhibit good chromaticity. Tb^{3+} -doped YAG and related garnet phosphors are typically synthesized by solid-state reaction of yttrium and aluminum oxides at temperatures in excess of 1550°C [3]. Conventional high temperature synthesis yields coarse particles that require grinding to achieve the desired particle size. It is possible to degrade the luminescent properties by the mechanical action of grinding, therefore the process must be precisely controlled [4,5]. The improvement of synthesis technique has been investigated as a possible means of increasing the efficiency of oxide phosphors for application in FEDs. It was the goal of this study to prepare various garnet phosphors via alternative synthesis routes such as hydrothermal and combustion synthesis and compare their low voltage efficiency data to those of solid-state reacted garnets.

Hydrothermal synthesis is a method to produce fine grained phosphors directly without grinding. Oxide phosphors prepared hydrothermally include $\text{Zn}_2\text{SiO}_4:\text{Mn}$ [6], $\text{YVO}_4:\text{Eu}$ [7], and $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Tb}$ [8]. The hydrothermal synthesis of submicron YAG:Tb powders with cathodoluminescent properties similar to those of YAG:Tb prepared via high temperature routes, has been reported [1]. Combustion synthesis is a technique commonly used to produce multicomponent oxide ceramics. The process involves the highly exothermic redox reaction of metal nitrate-carbonaceous fuel precursors. We are the first to apply this technique to the synthesis of luminescent oxides [9]. In this work, we report the hydrothermal synthesis and combustion synthesis of the following garnet phosphors: $\text{Y}_3\text{Ga}_5\text{O}_{12}:\text{Tb}$ (YGG:Tb) and YAG:Tb.

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EXPERIMENT

Synthesis of Phosphors

The starting materials used for the hydrothermal synthesis of YAG:Tb and YGG:Tb were $\text{Y}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ (Aldrich), $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Johnson Matthey), $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (Baker) and/or $\text{Ga}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Aldrich). The appropriate nitrates were dissolved in water and 27% aqueous NH_3 was added until a pH of 10 was reached. The resulting gels were filtered, dried at 150°C , and fired at 500°C for 6h in N_2 gas. The amorphous precursors were then ground, individually welded in Au tubes with an equivalent weight of water, and autoclaved (Leco Tem-Pres) at 600°C and 3.2 MPa. Products were recovered by filtration, using Gelman $0.22\text{ }\mu\text{m}$ membrane filters, and heat treated at 1200°C .

For combustion synthesis, the starting materials $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Alfa REacton 99.99%), $\text{Al}(\text{NO}_3)_3$ (Alfa Aesar 99.999%), $\text{Ga}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Aldrich) and $\text{Tb}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Alfa Puratronic 99.999%) were mixed with the appropriate amount of carbohydrazide, $\text{CH}_6\text{N}_4\text{O}$ fuel (Aldrich), dissolved in deionized water, placed in a 300 mL Pyrex dish, and introduced into a muffle furnace preheated to 500°C . After combustion, powders were crushed in a mortar and pestle and heat treated for 1-2h at 1000 - 1600°C .

Phosphors were also prepared via solid-state reaction of stoichiometric amounts of Y_2O_3 (Aldrich), $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Johnson Matthey), Al_2O_3 (Ceralox), or Ga_2O_3 (Fluka) at 1200°C for 18h, followed by a grinding step and a final heat treatment at 1450°C for 6h.

Phosphor Characterization

Particle size was determined by scanning electron microscopy (SEM) using a Cambridge 360 microscope. Samples were sputtered with Au before analysis. Cathodoluminescence data were collected from samples packed approximately 1mm deep into stainless steel cups. The samples were placed in a vacuum chamber which was evacuated to a pressure of less than 5×10^{-6} Pa. A hot filament, low energy electron gun (Kimball Physics) was the source of the beam, which was steered and focused using external Helmholtz coils. During analysis the sample cup was maintained at a potential of +100 V with respect to ground. The electron beam was focused onto a spot 5.6 mm in diameter. Luminous intensity of the light emitted from the sample was measured with a Minolta CS-100 photometer.

RESULTS

As a result of hydrothermal processing, the amorphous precursor gels crystallized to form pure YAG:Tb and YGG:Tb powders. The YAG:Tb powder consisted of well formed crystallites with a garnet habit as shown in the SEM micrograph of Figure 1. Particle diameters were between 0.2 and $2\text{ }\mu\text{m}$, with a median diameter of $0.55\text{ }\mu\text{m}$. The garnet morphology of YGG:Tb was less defined. This is most likely a result of over-nucleation of the precursor gel, due to firing at an excessively high temperature. The particle size is similar to that of YAG:Tb, with a median particle diameter of $1\text{ }\mu\text{m}$. Combustion synthesis yielded a continuous, porous network of powders. The particles which make up this network are typically interconnected, forming agglomerates that are easily broken up with light grinding. The presence of pores and voids in the as-synthesized powders is a result of the escaping gaseous products during combustion. Figure 2 shows as-synthesized YGG:Tb particles that are not part of the porous network. These particles have diameters less than $1\text{ }\mu\text{m}$. After heat treatment to 1400°C for 2h, the individual particles began to sinter and form necks, as shown in Figure 3.

Figure 1. SEM micrograph of hydrothermally synthesized YAG:Tb powder.

Figure 2. SEM micrograph of combustion synthesized YGG:Tb particles in the as-reacted state.

Figure 3. SEM micrograph of combustion synthesized YGG:Tb heat treated at 1400°C 2h.

Low-voltage (200-1000 V) cathodoluminescent efficiency data were collected for solid-state, hydrothermal, and combustion synthesized YAG:Tb and YGG:Tb, at a constant power of 15 μ W. Figure 5 shows the efficiency in lumens per watt (lm/W) as a function of electron accelerating voltage for YAG:Tb made by each of the three techniques. The efficiencies for all three phosphors were essentially the same at voltages below 600 V. At these voltages, the penetration depth of the incident electron beam is low, exciting the surface layer of the phosphor particles. In the higher voltage regime, (>600 V), the penetration depth of the electron beam is greater and therefore penetrates deeper into the phosphor particles. The efficiencies of solid state and hydrothermal YAG:Tb at these voltages were approximately 0.5 lm/W greater than combustion synthesized YAG:Tb. It is likely that the combustion synthesized phosphor particles are disordered below the surface layer, hence there is a slight loss of efficiency. This disorder may be a result of the non-equilibrium nature of rapid exothermic reactions.

Figure 5. Effect of synthesis route on the CL efficiency of YAG:Tb phosphors.

The saturation resistance of hydrothermal garnets is superior to that of solid-state garnets. Saturation data at high power densities (up to 0.15 W/cm^2) were collected for YGG:Tb at a constant voltage of 600 V. These data are pictured in Figure 6. Though less efficient than the solid-state reacted powder, hydrothermal YGG:Tb retains a larger fraction of its original efficiency after exposure to maximum beam power. Solid-state YGG:Tb sustained more permanent damage, as measured by the loss of efficiency at low power densities. It is possible that YGG:Tb crystallites distribute heat and surface charge more uniformly, reducing the intensity of hot zones.

Figure 6. Saturation/burn data for YGG:Tb at 600 V.

CONCLUSIONS

YAG:Tb and YGG:Tb were prepared by hydrothermal, combustion, and solid-state synthesis. The low-voltage efficiency was not appreciably affected by synthetic route at 600 V and below. The differences in efficiency of the YAG:Tb prepared by the three techniques was more pronounced in the 600-1000 V regime. Each process yields phosphors with different physical properties. Smaller, well formed crystallites that are more resistant to burn at high power densities are obtained via hydrothermal synthesis. Combustion synthesized powders are porous networks in the as-synthesized condition. Fine grain size phosphors attainable via hydrothermal synthesis would benefit deposition of screens for FEDs. For optimal screen performance, combustion synthesized powders must be separated prior to deposition.

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