

10.2: Garnet Phosphors Prepared via Hydrothermal Synthesis

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Abstract

This project studied hydrothermal synthesis as a route to producing green-emitting cathodoluminescent phosphors isostructural with yttrium aluminum garnet ($\text{Y}_3\text{Al}_5\text{O}_{12}$, or YAG). Aqueous precipitation of Y, Gd, Al, Ga, and Tb salts produced amorphous gels, which were heated with water at 600 °C and 3200 bar to produce crystalline YAG:Tb, $\text{Y}_3\text{Ga}_5\text{O}_{12}$:Tb, $\text{Y}_3\text{Al}_3\text{Ga}_2\text{O}_{12}$:Tb, and $\text{Gd}_3\text{Ga}_5\text{O}_{12}$:Tb powders. Process parameters were identified that yielded submicron YAG:Tb and $\text{Y}_3\text{Ga}_5\text{O}_{12}$:Tb powders without grinding. Cathodoluminescent efficiencies were measured as functions of power density at 600 V, using both the hydrothermal garnets and identical phosphor compositions synthesized at high temperatures. Saturation behavior was independent of synthetic technique, however, the hydrothermal phosphors were less susceptible to damage (irreversible efficiency loss) at very high power densities (up to 0.1 W/cm²). The fine grain sizes available with hydrothermal synthesis make it an attractive method for preparing garnet phosphors for field emission, projection, and head-up displays.

Introduction

Field emission-based displays (FEDs) are emerging as alternatives to liquid crystal displays in direct-view flat panel display applications. FEDs use electron beams to excite cathodoluminescent (CL) phosphors deposited on a screen, as do conventional cathode ray tubes (CRTs). However, FEDs emit electrons from arrays of microscopic cold cathodes, rather than from thermionic electron guns such as those used in CRTs. Because the individual electron beams cannot be steered, the emitter array must be placed close to the phosphor screen (ca. 40-100 μm) to maintain adequate resolution. The emitter cathodes must therefore be operated at low voltages, potentially between 5 and 500 V, to avoid vacuum breakdown, which can occur at potential gradients in excess of 10⁵ V/cm.¹

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The low electron energies, high beam currents, and short cathode-screen distances in FEDs place new demands on phosphor screens. These demands are not well addressed by screens optimized for high energy CL displays such as CRTs. Phosphors for FED screens must be efficient at low voltages, and resistant to saturation and Coulomb aging at high current densities. Additionally, the phosphors must not contaminate the atmosphere within the FED by releasing volatile components. Other desirable characteristics include high chromatic saturation, short-to-medium persistence, electrical conductivity, and availability as fine-grained powders with a narrow size distribution. Improvements in saturation characteristics, damage resistance and grain size distribution would also benefit projection television and head-up displays, which require high screen brightness and resolution.²

Phosphors under consideration for use in FEDs include ZnS:Ag,Cl, ZnS:Cu,Al, and $\text{Y}_2\text{O}_3\text{S:Eu}$, which are used as the blue, green, and red elements in color television, respectively. Unfortunately, under certain conditions sulfide phosphors can generate sulfur-containing gases, which in turn can contaminate emitter cathodes.³ Oxide phosphors are preferable from a contamination standpoint, but the CL efficiencies of these materials are generally lower than those of sulfides. Reduced zinc oxide (ZnO:Zn) is unusual among oxide phosphors in that it is both efficient at low voltages (as low as 5 V) and electrically conductive,⁴ and it is being widely studied as a green-emitting phosphor for FEDs. However, the temperature sensitivity, and poor chromaticity and saturation characteristics of ZnO:Zn render it less than ideal in this application. In contrast, green-emitting garnet phosphors such as $\text{Y}_3\text{Al}_5\text{O}_{12}$:Tb (YAG:Tb) display good chromaticity, and high resistance to saturation and degradation at high power densities. These phosphors have efficiencies comparable to or greater than ZnO:Zn at moderate voltages (200-1000 V).⁵

YAG:Tb and related garnet phosphors such as $\text{Y}_3\text{Al}_3\text{Ga}_2\text{O}_{12}$:Tb (YAGG:Tb) are usually synthesized directly from the constituent oxides or oxide precursors at high temperatures (>1200 °C).⁶ This process produces grains several micrometers in diameter. These particles can be further reduced by grinding, but this can cause surface contamination and defects, decreasing efficiency.⁷ Hydrothermal synthesis has been used to

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produce fine grained ceramic powders without grinding, and hydrothermal routes have been reported for several oxide phosphors or phosphor host phases, including $\text{Zn}_2\text{SiO}_4\text{:Mn}$,⁸ $\text{YVO}_4\text{:Eu}$,⁹ and $\text{Y}_3\text{Al}_5\text{O}_{12}\text{:Tb}$.¹⁰

We have previously shown that this approach can be used to generate submicron YAG:Tb powders with CL characteristics similar to those of YAG:Tb prepared via conventional means.¹¹ We have since broadened this study to include garnet phosphors isostructural with YAG:Tb, in particular, $\text{Y}_3\text{Al}_3\text{Ga}_2\text{O}_{12}\text{:Tb}$ (YAGG:Tb), $\text{Y}_3\text{Ga}_5\text{O}_{12}\text{:Tb}$ (YGG:Tb), and $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ (GGG:Tb). We report here the hydrothermal synthesis of these phases for the first time, and discuss the effects of hydrothermal and high-temperature processing on CL parameters that are relevant to field emission displays.

Experimental

The YAG:Tb, YGG:Tb, GGG:Tb, and YAGG:Tb phosphors were synthesized hydrothermally by dissolving $\text{Y}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ or $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Aldrich) with $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (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) in water, then adding 27% aqueous NH_3 (Fisher) until a pH of 10 was reached. The resulting gels were then centrifuged, rinsed, dried at 175 °C, and heated at 500 °C for 12 h in flowing O_2 . This yielded amorphous precursors that were then ground, individually welded in Au tubes with an equivalent weight of water, and autoclaved at 600 °C and 3.2 MPa. Products were recovered by filtration, using Gelman 0.22 μm membrane filters, then annealed at 1200 °C.

YAG:Tb, YGG:Tb, and GGG:Tb powders were also synthesized via direct solid state reactions. Y_2O_3 or Gd_2O_3 (Aldrich), $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, and $\gamma\text{-Al}_2\text{O}_3$ (Ceralox) or Ga_2O_3 (Fluka) were combined in stoichiometric proportions, pre-reacted at 1200 °C for 18 h, reground, and annealed at 1450 °C for 6 h.

The purity of all phases was established by powder X-ray diffraction, using an Siemens D-500 diffractometer ($\text{Cu K}\alpha$ radiation, $\lambda = 1.54059 \text{ \AA}$). Particle sizes were determined by scanning electron microscopy (SEM) and by sedimentation. Samples for SEM were sputtered with Au, and analyzed using an AMRAY model 1645 electron microscope. Particle size determination by sedimentation was performed by suspending the powder samples in a 1 weight percent aqueous sodium hexametaphosphate solution or in ethylene glycol, sonicating, and measuring settling rates using a Horiba CAPA-700 particle size analyzer.

Cathodoluminescence data were collected from samples apcked approximately 1 mm deep into stainless steel

cups. The samples were installed 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 or screen surface 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 and chromaticity of the light emitted from the sample was measured with a Minolta CS-100 photometer.

Results

YAG:Tb As a result of hydrothermal processing, the amorphous precursor gel crystallized to form a pure YAG:Tb powder. This powder consisted of garnet-shaped YAG:Tb crystallites with particle diameters between 0.2 and 2 μm (Figure 1), and a median particle diameter of 0.55 μm . These crystallites showed little tendency to agglomerate, and could be readily suspended in water through sonication.

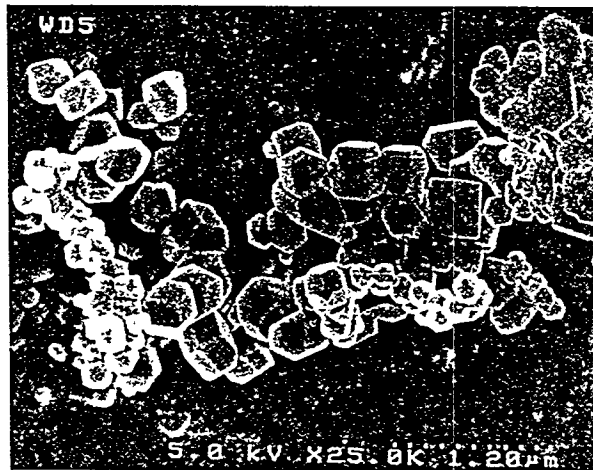


Figure 1: Hydrothermally synthesized YAG:Tb crystallites. Scale bar = 1.20 μm .

Portions of the YAG:Tb powders were annealed at 1200 °C and at 1450 °C for several hours. After annealing at 1200 °C, most crystallites remain intact, but those smaller than 0.1 μm sinter together. At 1450 °C, crystallites of all sizes begin to sinter together to yield a powder with a coarse, grainy texture as seen in SEM, but no additional improvement in CL efficiency is observed.

Cathodoluminescent efficiency data were measured as a function of power density for both solid state synthesized and hydrothermally synthesized YAG:Tb phosphors (Figure 2). This was accomplished by increasing the electron beam current at constant voltage to a maximum, then decreasing the current, while

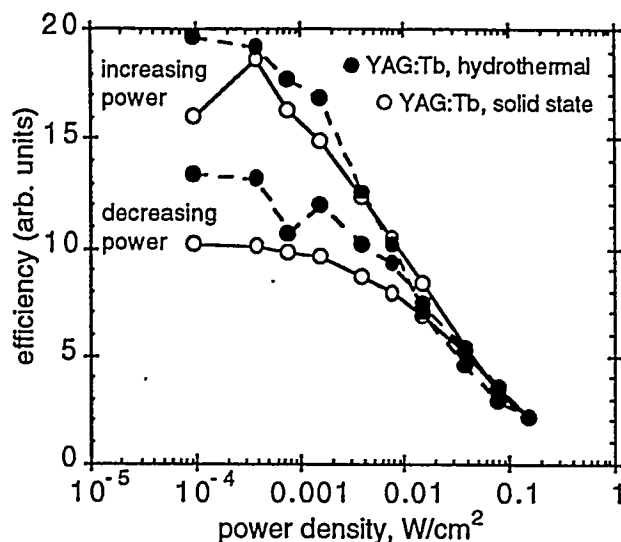


Figure 2: CL saturation/burn data for YAG:Tb phosphors at 600 V.

maintaining the beam in the same position on the phosphor sample. These data show that the phosphors saturate at high power densities (up to 0.15 W/cm²), and that the solid state and hydrothermal powders saturate to a similar extent. However, the annealed hydrothermal phosphors sustained less permanent damage, as measured by loss of low-power efficiency, than those prepared by conventional solid state reaction. It is possible that the better-faceted hydrothermal YAG:Tb crystallites distribute heat and surface charge more evenly, reducing the number and intensity of hot spots.

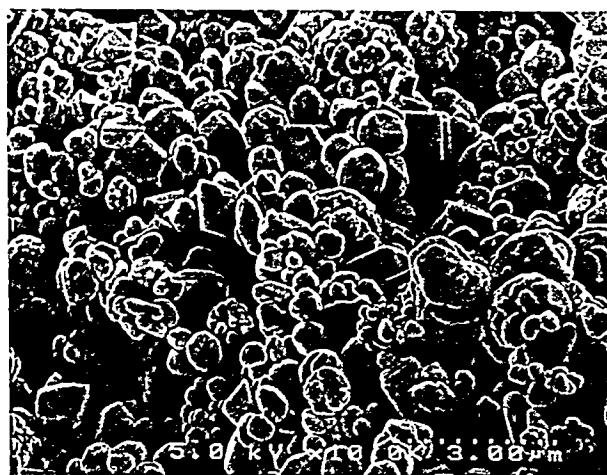


Figure 3: Hydrothermally synthesized YGG:Tb powder. Scale bar = 3 μm.

YGG:Tb The hydrothermal process also yielded pure Y₃Ga₅O₁₂:Tb powder, but the garnet morphology of

these grains is less distinct (Figure 3). This is consistent with mild over-nucleation of the starting gel, indicating that the gel had been pre-fired at an excessively high temperature. The particle size distribution is similar to that of YAG:Tb, with a median diameter of 1.0 μm. CL saturation and damage data were acquired in the same fashion as for YAG:Tb (Figure 4). While the sample of YGG:Tb prepared hydrothermally is generally less efficient than the sample synthesized at high temperature, the former appears more resistant to saturation at moderate power densities. In addition, the hydrothermal sample retains a larger fraction of its original efficiency after exposure to maximum beam power; this is consistent with the YAG:Tb results. It is possible that incomplete annealing may explain the lower initial CL efficiency of the hydrothermally prepared material.

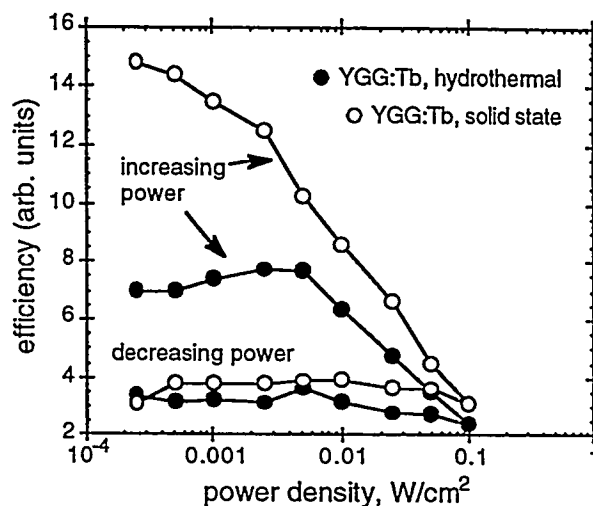


Figure 4: CL saturation/burn data for YGG:Tb phosphors at 600 V.

The 1931 CIE chromaticity coordinates changed slightly as the power density was increased, but emission generally remained a well-saturated green. The starting values of $x=0.351$, $y=0.527$ (solid state) and $x=0.350$, $y=0.525$ (hydrothermal) decreased to $x=0.353$, $y=0.517$ (solid state) and $x=0.343$, $y=0.523$ (hydrothermal) at maximum current density. The chromaticity coordinates reverted to their original values as the current density was reduced.

YAGG:Tb The hydrothermal process yielded grains of Y₃Al₃Ga₂O₁₂:Tb with a garnet habit (Figure 5) and a median particle diameter of 17 μm. CL saturation and damage data for this material are compared with those of a commercial sample of YAGG:Tb (Phosphor Technology Ltd.) in Figure 6. While the saturation behaviors are similar, the CL efficiency of the hydrothermal sample is generally twice that of the

commercial material, though the larger grain size may be partially responsible. The chromaticity coordinates changed reversibly with current density in a manner similar that seen in YGG:Tb.



Figure 5: Hydrothermally synthesized YAGG:Tb grains. Scale bar = 30 μm .

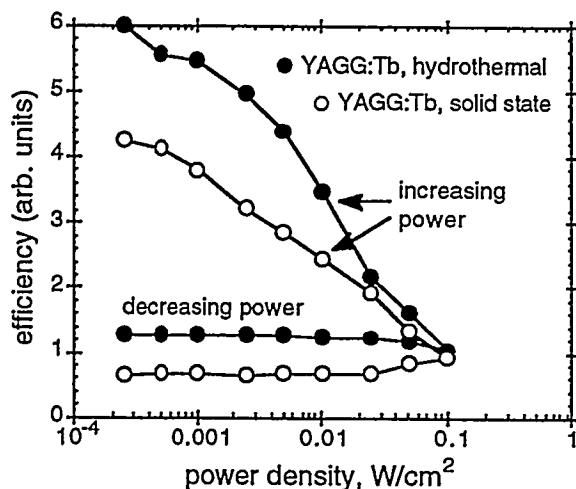


Figure 6: CL saturation/burn data for YAGG:Tb phosphors at 600 V.

GGG:Tb Gel compositions that yielded pure GGG:Tb upon hydrothermal treatment were identified, but the particle morphology is indistinct, with a median particle size of 3.2 μm . It is likely that the starting gels become over-nucleated at a firing temperature of 500 $^{\circ}\text{C}$. The CL data for GGG:Tb follow the same trend as those for YGG:Tb, specifically, the samples synthesized at high temperature are initially more efficient, but the hydrothermal samples retain a larger proportion of their initial efficiency.

Discussion

The fine grain sizes available with hydrothermal synthesis make it an attractive and enhanced method for preparing garnet phosphors for display applications where particle size is an issue. The particle size distribution can be controlled to a certain extent by altering process parameters. These parameters have nearly been optimized in the case of YAG:Tb and YGG:Tb synthesis, and are under study in YAGG:Tb and GGG:Tb. Small grain sizes facilitate electrophoretic deposition of screens for field emission displays, and increase resolution in projection and head-up display screens. These high-brightness displays may also benefit from the enhanced damage resistance of hydrothermal garnet phosphors. The CL results in this work suggest that terbium-doped garnets are efficient enough at moderate voltages (200-1000 V) to merit serious consideration as alternatives to $\text{Gd}_2\text{O}_2\text{S:Tb}$ and ZnO:Zn in field emission displays.

Acknowledgments

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