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Conf-951033--10

SAND95-1640C

EFFECTS OF PROCESSING ON THE LOW-VOLTAGE PERFORMANCE OF CATHODOLUMINESCENT GARNET PHOSPHORS

Mark L. F. Phillips* and Lauren E. Shea†
Ceramic Synthesis and Inorganic Chemistry Department
Sandia National Laboratories, Albuquerque, NM 87185

ABSTRACT

Field emission flat panel displays place new demands on the performance of cathodoluminescent phosphors. In particular, such phosphors must be efficient at lower voltages (ca. 100-1000 V), and must withstand higher current densities than are present on cathode ray tube screens. ZnO:Zn has been studied extensively as a low-voltage phosphor, but problems such as poor chromatic saturation and temperature sensitivity of emission remain. In this work the use of terbium-doped garnet phases such as yttrium aluminum garnet (YAG) and gadolinium gallium garnet (GGG) as low voltage green-emitting phosphors is evaluated. Hydrothermal synthesis yields well-faceted YAG grains with particle diameters of less than 1 μm. Cathodoluminescent efficiency at a particular voltage was not affected by synthetic route, though the hydrothermally synthesized material was less susceptible to damage at high power densities. An efficiency of 3.5 lm/W was observed for GGG:Tb at 800 V. Deposition of the phosphors onto conducting screens increased their efficiencies at very low voltages (< 200 V). These materials may be considered alternatives to reduced zinc oxide as green-emitting phosphors.

KEY WORDS: Hydrothermal, phosphors, displays

1. INTRODUCTION

Field emission-based flat panel displays (FEDs) are expected to realize several advantages over liquid crystal displays (LCDs). These include lower power consumption, lower manufacturing costs, increased range of viewing angles, and enhanced resolution and brightness. FEDs use electron beams to excite cathodoluminescent (CL) phosphors deposited on a screen, as do conventional cathode ray tube (CRT) displays. However, FEDs differ from CRTs in that they use arrays of microscopic cold cathodes to irradiate a phosphor screen, rather than thermionic electron guns. FEDs also operate at lower voltages (100-1000V, rather than 10-25 keV for CRTs), principally to avoid vacuum breakdown.[1]

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* Author to whom correspondence should be addresed.
† Permanent address: Department of Applied Mechanics and Engineering Sciences, University of California, San Diego; La Jolla, CA 92093-0418.

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FEDs operating in full color require low voltage phosphors in three colors, namely, red, green, and blue. In order to compete with LCDs in terms of power consumption, the FED phosphor screen will require a white brightness efficiency of approximately 2-3 lumens per watt. In a 3-color scheme with good color saturation the necessary individual efficiencies are approximately 6 lm/w for the green phosphor, 3 lm/W for the red phosphor, and 1 lm/W for the blue phosphor. Other requirements include high saturation power, short or medium short persistence, and long lifetime. These properties can be achieved in sulfide phosphors,[2] but sulfides carry a risk of contamination,[3] which can damage field emitters.[4] Oxide phosphors are less likely to contaminate the atmosphere within the FED, but few oxide phosphors yield efficiencies as high as those of the sulfides.

Reduced zinc oxide (ZnO:Zn) is unusual among oxide phosphors in that it is both highly efficient (13 lm/W)[5] and electrically conductive, and it is being widely studied as a green-emitting phosphor for FEDs. However, the poor chromaticity, low saturation power, and temperature sensitivity of ZnO:Zn render it less than ideal in this application. Green-emitting garnet phosphors such as YAG:Tb have good chromaticity, high saturation power and resistance to degradation at high power densities; these attributes make these materials useful in projection CRT screens.[6] Unfortunately, the efficiencies of these phosphors at low voltages are significantly less than that of ZnO:Zn.

Two problems that limit efficiency of insulating phosphors at low voltage are surface bound electrons (SBEs) and surface recombinant (SR) centers.[7] SBEs result from secondary electron emission and cause the surface of the phosphor grain to acquire a negative charge, which repels or deflects the incident electron beam. SR centers are surface defects at which excitations created by electron impact can decay nonradiatively. Grinding phosphors can introduce SR centers by contaminating the grain surface or causing defects.[8]

These problems might be dealt with by directly synthesizing phosphors with the proper grain size, eliminating the requirement for grinding, and by improving the conductivity of the particle surface. Hydrothermal synthesis is a route to producing well-crystallized oxide powders with good control over particle size distribution that has been demonstrated previously in YAG.[9] This technique, in combination with coating the phosphor grain onto a conductive screen, may improve efficiency at low voltages by simultaneously reducing the concentrations of SR centers and SBEs on the grain surface.

In this work, the potential of Tb^{3+}-activated garnets as efficient green-emitting low voltage phosphors suitable for FED use is evaluated. YAG:Tb phosphors were prepared by both conventional solid state reaction and hydrothermal synthesis techniques in order to determine the effects of synthetic method on physical properties such as particle size and morphology. CL data were acquired from 100 to 1000 V by directly exciting the surface of packed powders and by exciting a thin layer of phosphor deposited onto conductive glass substrates. These results were used to determine the influence of synthesis and deposition on the low-voltage CL efficiency and power saturation characteristics of these materials.

2. EXPERIMENTAL

$Y_{3-x}Tb_xAl_5O_{12}$ (YAG:Tb) and $Gd_{3-x}Tb_xGa_5O_{12}$ (GGG:Tb) powders were prepared by direct solid state reaction: Y_2O_3 (or Gd_2O_3), $Tb(NO_3)_3 \cdot 5H_2O$, and $Al(OH)_3$ (or Ga_2O_3) were combined in stoichiometric proportion, pre-reacted at 1200 °C for 18 h, reground, and annealed at 1450 °C for 6 h. The YAG:Tb compositions were also synthesized hydrothermally by dissolving nitrate salts of Y, Al, and Tb in water, then adding aqueous NH_3 until a pH of 10 was reached. The resulting gels were then filtered, dried at 150 °C, and heated at 500 °C for 6 h in N_2. This yielded amorphous YAG:Tb precursors which were then ground, individually sealed in Au tubes with an equivalent weight of water, and autoclaved (Leco Tem-Pres) at 600 °C and 3.2 MPa for 24-32 hours. Products were recovered by filtration, using Gelman 0.22 μm membrane filters. Portions of the hydrothermally synthesized YAG:Tb samples were annealed at 1200 °C.

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 accomplished by suspending the powder samples in a 1 weight percent aqueous sodium hexametaphosphate solution, sonicating, and measuring settling rates using a Horiba CAPA-700 particle size analyzer. Crystallite sizes determined from X-ray line broadening were calculated using the Scherrer equation from the widths of the (420) line of $Y_3Al_5O_{12}$, using a LaB_6 standard. Powder X-ray diffraction (XRD) data were collected using a Scintag Pad V diffractometer.

Cathodoluminescence data were collected from samples packed ca. 1 mm deep into stainless steel cups, and from samples deposited onto conducting tin oxide-coated glass slides (Libbey-Owens-Ford). The samples were installed in a vacuum chamber, which was evacuated to a pressure of less than $5x10^{-6}$ 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 +30 V with respect to ground. The electron beam was focused onto a spot 4.5 mm in diameter. Light emitted from the sample was transmitted to a spectroradiometer (Oriel), which measured radiant energy as a function of wavelength.

3. RESULTS

Hydrothermal synthesis yielded YAG:Tb powders consisting of well-faceted grains with a garnet morphology (Figure 1). Particle diameters ranged from 0.2 and 1.0 μm, with the largest mass fraction lying between 0.4 and 0.5 μm. These crystallites showed little tendency to agglomerate, and could be readily suspended through sonication. Minor sintering of the smaller crystallites occurred upon annealing at 1200 °C, though grains larger than ca. 0.3 μm were unaffected.

Synthesis of YAG:Tb and GGG:Tb via the solid state yields larger, irregular grains that appear to be sintered microcrystallites. Particle size data show that grain diameters range principally from 2 to 7 μm, with the largest mass fraction between 5 and 6 μm. Crystallite sizes for the materials obtained from initial reaction at 1200 °C were calculated from X-ray line broadening data to be approximately 0.05 μm. Annealing at 1450 °C causes further sintering, yielding grains with an effective crystallite diameter of 0.3 μm (Figure 2).

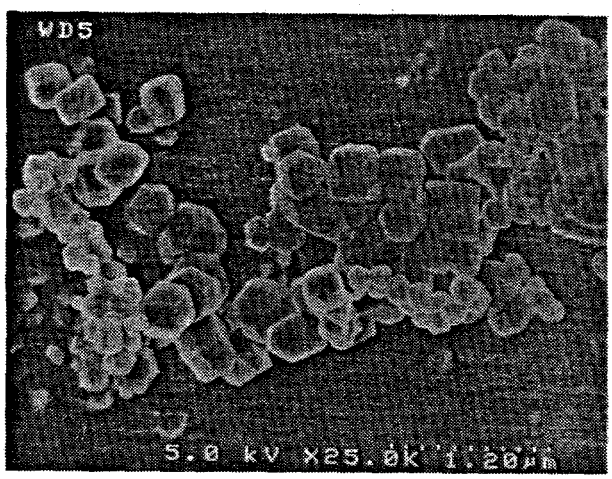

Figure 1: Hydrothermally synthesized YAG:Tb powders (scale bar = 1.2 μm).

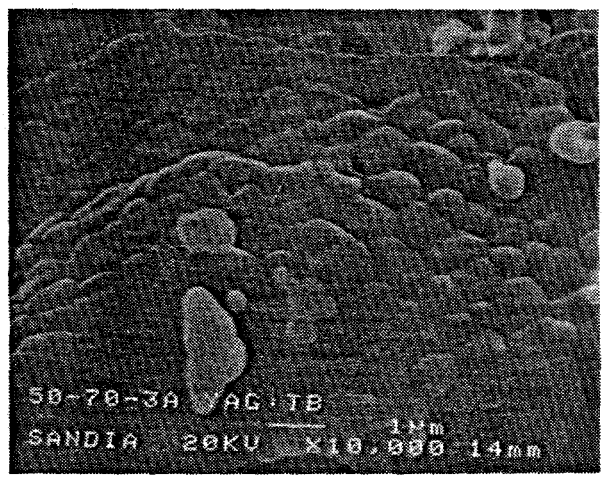

Figure 2: Solid state-reacted YAG:Tb grains, annealed at 1450 °C (scale bar = 1 μm).

CL efficiency data as a function of electron voltage at 1.5×10^{-5} W for packed YAG and GGG powders doped with 5 mole percent Tb are presented in Figure 3. In the range 150-1000V, CL efficiency increases with voltage at constant power, approximately doubling between 150 and 1000 V. The threshold voltage for all packed powders was between 100 and 150V. The efficiencies of solid state and hydrothermal YAG:Tb were similar to each other at all voltages, while those of GGG:Tb (solid state) were greater by approximately 0.5 lm/W. The dead voltage and steep slope of the efficiency vs. voltage curve are most likely due to surface bound electrons: at higher voltages, luminance is brighter at constant power due to increased penetration depth of the primary electron beam.

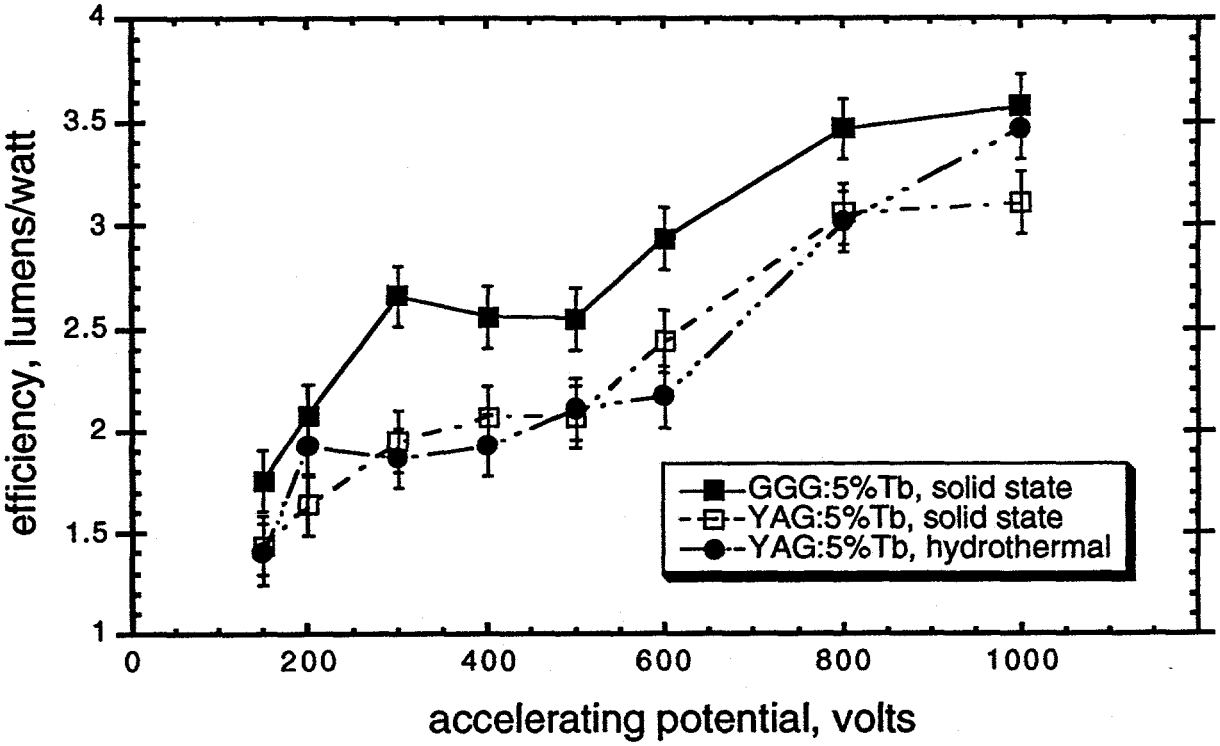

Figure 3: CL efficiencies for garnet phosphors, measured as packed powders.

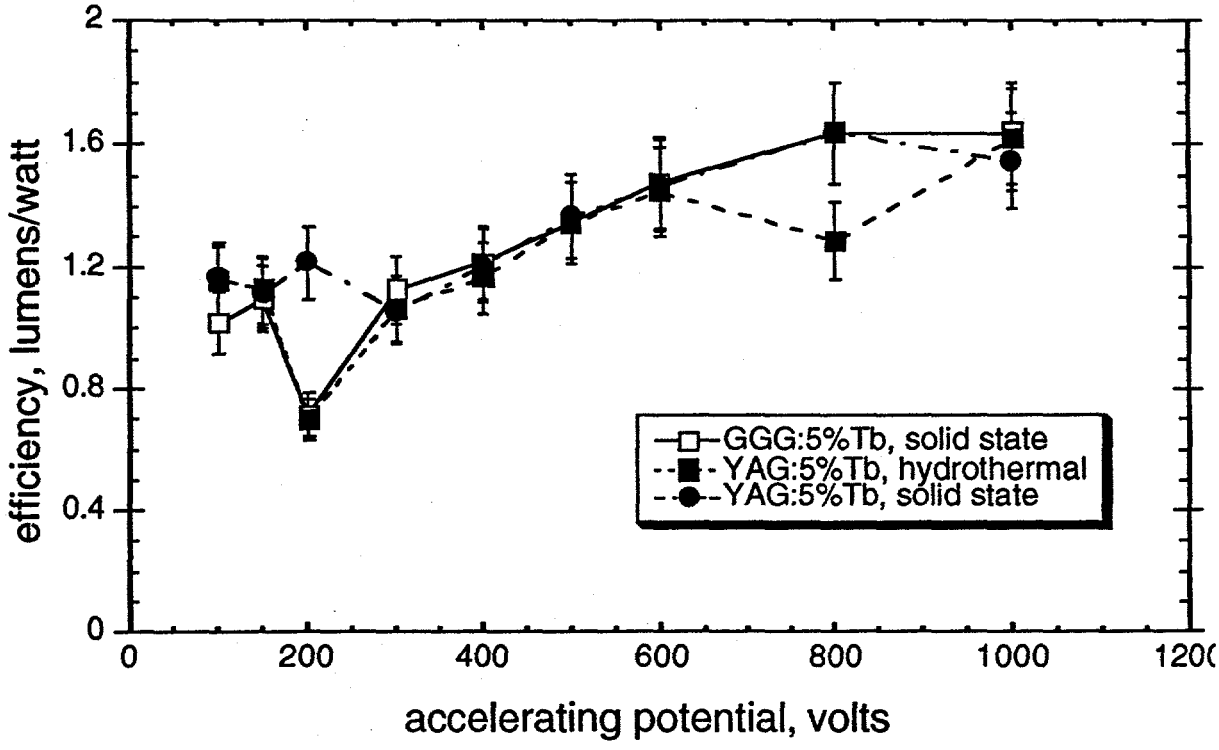

Figure 4: CL efficiencies for garnet phosphors deposited on conducting screens.

CL data at 15 μW are reported for screen-deposited phosphors in Figure 4. The screens tested were not completely covered with the phosphor grain, and not all phosphor grains were in contact with the conducting surface. Therefore, direct comparisons of the efficiencies of different screened samples, and of screened and powder samples, are not valid. It can nevertheless be seen that for a particular phosphor, screen deposition substantially improves efficiencies at low voltages (< 200 V), and has the overall effect of flattening the curve of efficiency vs. voltage with respect to the same curve for the packed powders.

A comparison of power saturation data measured with a continuous current at 600 V for solid state-synthesized and hydrothermally synthesized YAG:Tb phosphors is shown in Figure 5. These curves show that all of the phosphors tended to saturate at high power densities (up to 1500 W/m^2), and that the solid state and hydrothermal powders saturated to a similar extent. However, the hydrothermal phosphors that had been annealed 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 surface charge and heat more evenly, reducing the number and intensity of hot spots.

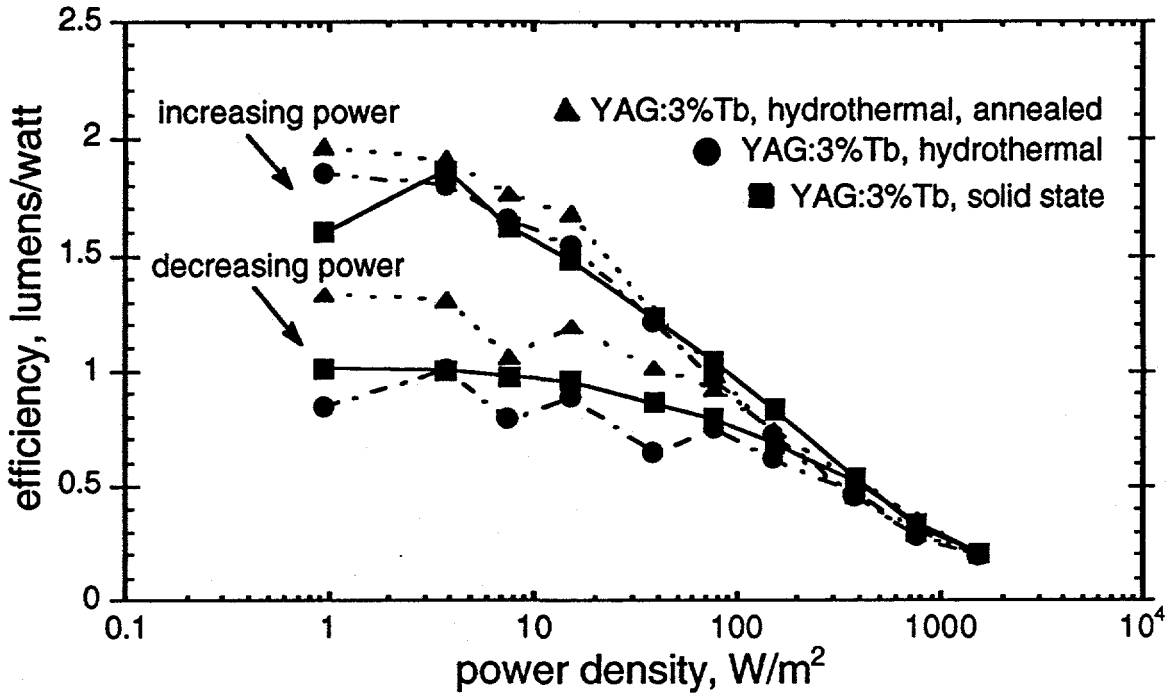

Figure 5: CL power saturation data for packed YAG phosphor powders at 600 V.

4. DISCUSSION

Hydrothermal synthesis can be considered an alternative to conventional high-temperature reaction in YAG:Tb phosphor manufacture, since it yields smaller, well formed crystallites that are more resistant to burn at high power densities. These attributes would most significantly benefit projection CRT displays, which currently employ YAG:Tb as green-emitting phosphors. Based on the relationships between efficiency and voltage in the CL data acquired on YAG:Tb phosphors in packed powder and screen forms, it is apparent that deposition technique has the most significant effect on efficiency at very low voltages (< 200 V). The improvement in threshold voltage and low-voltage efficiency of the phosphors upon deposition onto conducting screens indicates that surface bound electrons are principally responsible for limiting the CL performance of these materials below 500 V.

Improvements in screen deposition technique may further enhance the low-voltage CL characteristics of YAG:Tb and GGG:Tb. The high efficiencies of garnet phosphors, combined with their excellent chromaticities and power saturation properties, merit these materials serious consideration as green-emitting phosphors for field-emitter flat panel displays.

5. ACKNOWLEDGMENTS

This work was supported by the U. S. Department of Energy under contract no. DE-AC04-94AL85000. The contributions of R. J. Walko, G. R. Schuster, G. Zender and D. L. Lamppa are appreciated.

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