

The influence of processing parameters on luminescent oxides produced by combustion synthesis

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Abstract

Rare-earth activated oxide phosphors have application in high energy photoluminescent (plasma panels) and cathodoluminescent (field emission devices) flat panel displays. These phosphors are composed of a highly insulating host lattice with fluorescence arising from the $3d \rightarrow 3d$, $5d \rightarrow 4f$ or $4f \rightarrow 4f$ transitions in transition metal or rare earth ions. Fabrication of complex host compositions Y_2SiO_5 , $Y_3Al_5O_{12}$, Y_2O_3 , and $BaMgAl_{10}O_{27}$ along with controlled amounts of the activators (Cr^{3+} , Mn^{2+} , Ce^{3+} , Eu^{2+} , Eu^{3+} , Tb^{3+} , Tm^{3+}) represent a challenge to the materials synthesis community. High purity, compositionally uniform, single phase, small and uniform particle size powders are required for high resolution and high luminous efficiency in the new flat panel display developments. This paper will review the synthesis techniques and present physical and luminescent data on the resulting materials. © 1999 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

The visible-light-generating components of emissive, full color, flat panel displays are called phosphors. Phosphors are composed of an inert host lattice and an optically excited activator, typically a 3d or 4f electron metal. For application in the emerging full color, flat panel display industry, thermally stable, high luminous efficiency, radiation resistant, fine particle size powders are required. The demands of these newer technologies have produced a search for new materials and synthesis techniques to improve the performance of phosphors.

Oxide phosphors were found to be optimal for field emission display (FED) and plasma panel display (PDP) devices. Compared with a cathode ray tube, an FED operates with lower energy (3–10 keV) but higher current density (1 mA/cm²) beams impinging on the phosphors. This requires more luminous efficient and thermally stable materials. Luminous efficiency is defined as the ratio of the energy out (lumens) to the input energy. Outgassing from the highly efficient sulfide based phosphors has been shown to degrade the cathode tips of the field emitter array and cause irreversible damage [1]. For PDPs, high energy photons (147 nm, 8.5 eV) impinge on the phosphor powders and cause a

reduction in luminous efficiency of the display over time because of radiation damage induced in the material [2].

Another requirement is on the particle size distribution: there is a maximum and minimum particle size limitation to the powders. For FED applications, about five particle layers are required to achieve optimal light output [3]. Large particles ($> 8 \mu\text{m}$) require thicker layers, increasing the phosphor cost and also producing more light scattering. Additionally the pixel pitch ($\sim 250 \mu\text{m}$) places a maximum on particle size [4]. Alternatively, it was found that small particles ($< 0.2 \mu\text{m}$) do not have high luminous efficiency arising from grain boundary effects [5]. The activator ion in the crystal is most efficient when located in the bulk material in a regular crystal field. Activators located on the surface or on the grain boundaries are thought to be non-luminescent or even luminescence quenching regions.

For full color displays, three phosphor compositions are necessary to emit in the red (611–650 nm), green (530–580 nm) and blue (420–450 nm) regions of the visible spectrum. Some oxide based phosphors used in FEDs are the red-emitting $(Y_{1-x}Eu_x)_2O_3$, the green-emitting $(Y_{1-x}Tb_x)_3Al_5O_{12}$ and the blue-emitting $(Y_{1-x}Ce_x)_2SiO_5$ [6]. For some PDPs the red-emitting component is $(Y_{1-x}Eu_x)_2O_3$, the green-emitting is $Zn_{1-x}Mn_xSi_2O_5$ and the blue-emitting is $(Ba_{1-x}Eu_x)MgAl_{10}O_{17}$ [7]. Sulfide phosphors are also used in FEDs but suffer from the aforementioned degradation problems.

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Table 1
Phosphor compositions obtained by combustion synthesis

Color	Composition	Peak wavelength (nm)
Red-emitting	(Y _{1-x} Eu _x) ₂ O ₃	611
	(Y _{1-x} Eu _x) ₃ Al ₅ O ₁₂	590
Green emitting	(Y _{1-x} Tb _x) ₃ Al ₅ O ₁₂	545
Blue emitting	(Ba _{1-x} Eu _x)Mg ₂ Al ₁₆ O ₂₇	450
	(Ba _{1-x} Eu _x)MgAl ₁₀ O ₁₆	450
	ZnGa ₂ O ₄	400
	(Y _{1-x} Tm _x) ₃ Al ₅ O ₁₂	460–470
	(Y _{1-x} Ce _x) ₂ SiO ₅	395, 423

2. Phosphor synthesis techniques

Synthesis of oxide phosphors has been achieved by a variety of routes: solid-state reactions [8,9], sol–gel techniques [10], hydroxide precipitation [11], hydrothermal synthesis [12,13] and combustion synthesis [14–17]. Solid-state reactions are performed at high temperatures, typically around 1600°C, because of the refractory nature of the oxide precursors. For multielement compositions, an incomplete reaction is often obtained with undesirable precursor products present in the final product. This technique requires several heating and grinding steps in order to achieve well-reacted, small particle size phosphors. For sol–gel and hydroxide precipitation methods, dilute solutions of metallorganics or metal salts are reacted and condensed into an amorphous or weakly crystalline mass. The advantage of these methods is that atomically mixed powders are obtained in the as-synthesized condition and problems associated with incomplete reactions are avoided. However, these as-synthesized materials must also be heat treated to high temperatures to crystallize the desired phase and to achieve particle sizes greater than 0.2 μm. Hydrothermal synthesis is a low temperature and high pressure decomposition technique that produces fine, well-crystallized powders [13]. These powders must also be heat treated to high temperature to extract the maximum luminous efficiency. Combustion synthesis is a novel technique that has been applied to phosphor synthesis in the past few years. This technique produces highly crystalline powders in the as-synthesized state and will be described in more detail in Section 3.

3. Combustion synthesis of oxide phosphors

Combustion synthesis involves the exothermic reaction between metal nitrates and a fuel. Combustion synthesis is an important powder processing technique generally used to produce complex oxide ceramics such as aluminates [18–21], ferrites [22–25], and chromites [26,27]. The process involves the exothermic reaction of an oxidizer such as metal nitrates, ammonium nitrate, and ammonium perchlorate [28], and an organic fuel, typically urea (CH₄N₂O), carbonylhydrazide (CH₆N₄O), or glycine (C₂H₅NO₂).

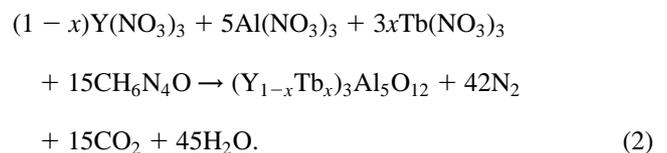
The combustion reaction is initiated in a muffle furnace or on a hot plate at temperatures of 500°C or less; much lower than the phase transition of the target material. In a typical reaction, the precursor mixture of water, metal nitrates, and fuel decomposes, dehydrates, and ruptures into a flame after about 3–5 min. The resultant product is a voluminous, foamy powder which occupies the entire volume of the reaction vessel. The chemical energy released from the exothermic reaction between the metal nitrates and fuel can rapidly heat the system to high temperatures (> 1600°C) without an external heat source. Combustion synthesized powders are generally more homogeneous, have fewer impurities, and have higher surface areas than powders prepared by conventional solid-state methods [28].

The mechanism of the combustion reaction is quite complex. The parameters that influence the reaction include: type of fuel, fuel to oxidizer ratio, use of excess oxidizer, ignition temperature, and water content of the precursor mixture. In general, a good fuel should react non-violently, produce non-toxic gases, and act as a complexant for metal cations [28]. Complexes increase the solubility of metal cations, thereby preventing preferential crystallization as the water in the precursor solution evaporates [29]. The adiabatic flame temperature, T_f , of the reaction is influenced by the type of fuel, fuel to oxidizer ratio, and the amount of water remaining in the precursor solution at the ignition temperature [27]. The flame temperature can be increased with the addition of excess oxidizer such as ammonium nitrate [28], or by increasing the fuel/oxidizer molar ratio. The following equation can be used to approximate the adiabatic flame temperature for a combustion reaction:

$$T_f = T_0 + \frac{\Delta H_r - \Delta H_p}{c_p}, \quad (1)$$

where ΔH_r and ΔH_p are the enthalpies of formation of the reactants and products, respectively, c_p is the heat capacity of products at constant pressure, and T_0 is 298 K. Measured flame temperatures are typically lower than calculated values of flame temperature as a result of heat loss. Table 1 lists the various phosphor compositions that were synthesized by combustion synthesis.

An example of a stoichiometric combustion reaction of yttrium, aluminum and terbium nitrate with carbonylhydrazide to form (Y_{1-x}Tb_x)₃Al₅O₁₂ is:



When complete combustion occurs, the only gaseous products obtained are N₂, CO₂, and H₂O, making this an environmentally clean processing technique. The generation of gaseous products increases the surface area of the powders by creating micro- and nanoporous regions. For

Table 2
Number of moles of gas produced for different fuels per mole of metal sesquioxide formed

Fuel	Reaction	No of moles of gas produced
Glycine	$2M(NO_3)_3 + 10/3C_2H_5NO_2 \rightarrow M_2O_3 + 20/3CO_2 + 25/3H_2O + 14/3N_2$	19.7
Urea	$2M(NO_3)_3 + 5CH_4N_2O \rightarrow M_2O_3 + 5CO_2 + 10H_2O + 8N_2$	23.0
Carbohydrazide	$2M(NO_3)_3 + 15/4CH_6N_4O \rightarrow M_2O_3 + 15/4CO_2 + 45/4H_2O + 21/2N_2$	25.5

the earlier reaction, for every mole of solid produced, 102 mol of gas are produced.

The difference in particle size with the use of different fuels depends upon the number of moles of gaseous products released during combustion. As more gases are liberated, the agglomerates are disintegrated and more heat is carried from the system thereby hindering particle growth. A greater number of moles of gas are produced in combustion reactions with carbohydrazide. If complete combustion is assumed, the gaseous product amounts liberated in combustion reactions with glycine, urea and carbohydrazide, are shown in Table 2. The reactions shown are for 2 mol of nitrate producing 1 mol of metal sesquioxide. If $Y_3Al_5O_{12}$ (YAG) is produced, the reactions must be multiplied by four, as 8 mol of nitrate are used in the reaction.

The BET surface area for the as-synthesized YAG phosphors made with glycine, urea and carbohydrazide was measured to be 19, 22 and 25 m²/g, respectively [16], which is consistent with the increase in number of moles of gas produced.

Fig. 1 shows the efficiency in lumens per watt (lm/W) as a function of electron accelerating voltage for $(Y_{1-x}Tb_x)Al_5O_{12}$ made by solid-state, hydrothermal synthesis and combustion synthesis. The combustion synthesized

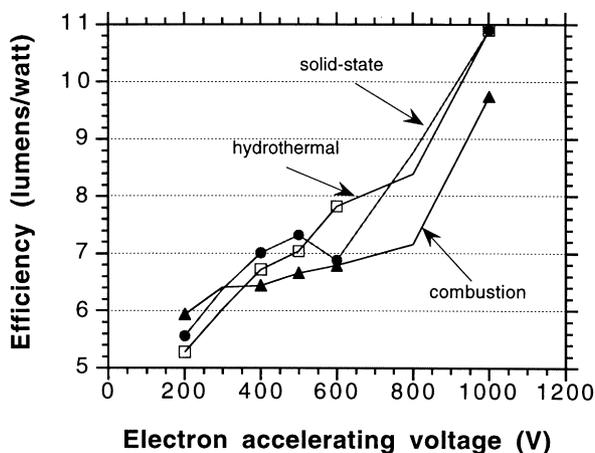


Fig. 1. Effect of synthetic route on the low-voltage cathodoluminescence efficiency of $(Y_{1-x}Tb_x)3Al_5O_{12}$.

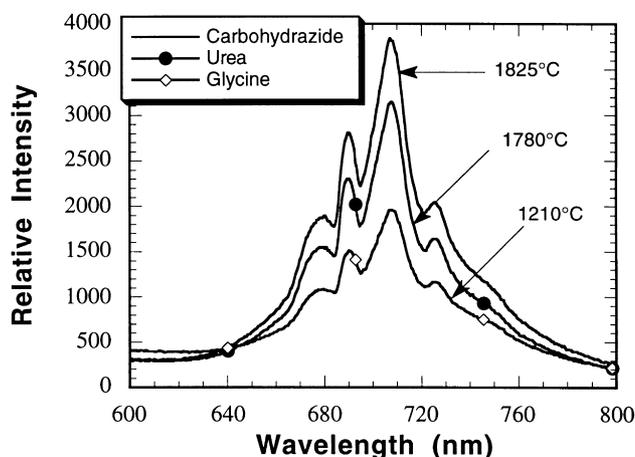


Fig. 2. Photoluminescence emission spectra and measured flame temperatures of $Y_3(Al_{1-x}Cr_x)_5O_{12}$ phosphors made with urea, carbohydrazide and glycine. 435 nm excitation.

YAG produced in this work has low-voltage cathodoluminescence efficiencies that are comparable to powders produced by other 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, (~ 0.004 nm at 600 V) exciting the surface layer of the phosphor particles. In the higher voltage regime, (> 600 V), the penetration depth of the electron beam is greater (~ 0.03 nm at 1 kV). The efficiencies of solid-state and hydrothermal synthesized $(Y_{1-x}Tb_x)Al_5O_{12}$ at these voltages were approximately 1.0 lm/W greater than combustion synthesized $(Y_{1-x}Tb_x)Al_5O_{12}$. This is because of the smaller crystallite size of these powders (~ 60 nm) compared with hydrothermal and solid-state synthesized powders (~ 100 nm).

Fig. 2 shows the photoluminescent (PL) emission spectra of $Y_3(Al_{1-x}Cr_x)_5O_{12}$ phosphors produced with carbohydrazide, glycine, and urea. The emission intensity increased with the measured flame temperature of the reaction. Carbohydrazide produced the highest flame temperature and also the highest PL emission intensity. This is an indication that certain properties of the resulting powders in the as-synthesized state, such as crystallite size or disorder of the local environment surrounding the activator ions, influenced the PL spectra.

4. Conclusions

Fabrication of multielement oxide phosphor compositions has created a need for new synthesis techniques. Combustion synthesis is an ideal technique used to produce fine, chemically homogeneous and pure, single phase powders in the as-synthesized condition. Smaller particle sizes were produced from reactions that liberated the greatest amount of gas. The highest luminescence emission intensity was correlated with the highest measured flame

temperature, indicating that thermal effects are important for producing optimally performing phosphor powders.

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