MICROWAVE SYNTHESIS AND PROCESSING OF PHOSPHORS

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ABSTRACT
Microwave synthesis and processing of phosphors was studied. The material systems studied in this work include [Ca10(PO4)6(Cl,F):Sb:Mn, Halo], (Y,Eu)2O3 (YOE), BaMgAl10O17:Eu (BAM), and (La,Ce)PO4:Ce:Tb (LAP), with or without flux. The microwave processing was carried out on a few chosen phosphors coated with oxides to prevent property degradation. All the experiments were conducted in a multimode microwave furnace of 2.45 GHz. The results show that most properties of the microwave-synthesized phosphors were comparable to that of the conventional products, although the kinetics of the synthesis was enhanced significantly. The soaking time at the final temperature was reduced by up to 90% over the conventional process. In addition, the required synthesis temperature was lowered by 100-200K. The microwave-synthesized unfluxed LAP showed substantial improvement in thermal stability. Several phosphors were coated with silica or alumina by a sol-gel method. The thickness of the coating layer varied between 0.1 to 0.5 µm. It was found that the luminescence decreased as the coating thickness increased, although the decrease with silica coated P-1 was only 2%. Microwave processed silica-coated samples showed better luminescence than the conventionally processed samples with the same coating.

KEYWORDS: microwave, synthesis, phosphor, processing, coating, luminescence

INTRODUCTION
Phosphors are important materials in lighting and display. Firing is a necessary step for solid-state phosphor synthesis since activation energy must be supplied for the activators to go into the crystal structure of the host material. By solid-state reaction, conventional synthesis of phosphors takes many hours even with flux. Microwave processing is a relatively new technique and characterized by substantially accelerated reaction kinetics in the material systems if properly chosen. Using microwave processing, various phosphors have been synthesized. The high efficiency phosphors developed for field emission displays, plasma displays, and white light emitting diodes (LED) tend to be degraded by the operating environment and/or the devices’ manufacturing conditions. Transparent oxide coating on phosphor powders is an effective approach to protecting phosphors from ageing. The coating can isolate the phosphor from the environment and could protect both the phosphor and the device. Here we report the microwave synthesis of some important phosphors and microwave processing of some phosphors coated with oxides.

EXPERIMENTAL
Microwave synthesis was carried out in a 2.45 GHz, 6 kW capability multimode microwave furnace, with atmosphere controlled, although, only about 1 kW or less power was needed in the experiments. The powder sample (30-70 g each) was loaded in an alumina crucible, which was then placed in a properly insulated package with SiC as microwave susceptor. The insulation package was made of porous FiberFrax Duraboard 3000. The temperature of the sample was monitored with an optical pyrometer. The temperature was controlled by adjusting input power. During the microwave processing, the sample was rotating horizontally about the axis. The samples were microwave heated up and held at the designed temperatures for typically 10-20 min. The microwave-synthesized products were characterized for particle size, brightness, phase composition, morphology, luminescence emission, and color coordinates.

Microwave processing of the oxide-coated phosphors was to devise protective coatings for phosphor grains which will isolate the phosphor from ion bombardment but remain transparent to
ultraviolet radiation. The requirement that the coatings be transparent in the 140-180 nm range restricts coating compositions to oxides of silicon, aluminum, and the alkaline earths. The coating was composed of either silica gel, or alumina gel. The experiments of microwave processing of the coating were carried out in the microwave furnace at 1 kW. Three phosphors, Sylvania 2291, (Ce,Tb)MgAl$_{11}$O$_{19}$ (CAT, with a BET surface area of 0.67 m$^2$/g), Sylvania 2461 (BAM, 0.88 m$^2$/g), and DuPont Zn$_2$SiO$_4$:Mn$^{2+}$ (P-1, 0.70 m$^2$/g) were selected for coating study.

Silica gels were prepared at room temperature by mixing tetraethyl orthosilicate (TEOS, Fisher Scientific Co., Fair Lawn, NJ), ethyl alcohol (Pharmco Products Inc., 200 proof), de-ionized water, and hydrofluoric acid (J.T. Baker Chem. Co., Phillipsburg, NJ, 48-51%) in the mole ratio of 1:4:4:0.05. Among them ethyl alcohol was used as solvent, and hydrofluoric acid as a catalyst. Silica gel was formed through hydrolysis and condensation.

The phosphor powders to be coated were wetted and dispersed in alcohol by ultrasound waves of 20 kHz. Excessive alcohol was then removed and the gel solution was added to the dispersed powders. This mixture was partially exposed to air to allow the solvent, water, and the catalyst to evaporate. Gelation occurred hours later and the phosphor particles were coated with a layer of silica gel. The amount of the solution was controlled to get various coating thicknesses.

The microstructure of the gel-coated phosphors was characterized by scanning electron microscopy (SEM, ISI-DS 130), phase composition by powder X-ray diffraction (XRD) using Cu K$\alpha_1$ radiation on a Scintag diffractometer (Scintag, Sunnyvale, CA), and the luminescence was checked using a F-400 Fluorescence Spectrophotometer (Hitachi). The luminescence emission at wavelength 545 nm (for CAT) and 450 nm (for BAM) was tested on uncoated and coated samples, and that at 525 nm was tested on P-1.

RESULTS AND DISCUSSION

Microwave Synthesis

Halo was synthesized by microwave processing from a mixture of HCaPO$_4$, CaCO$_3$, CaF$_2$, NH$_4$Cl, MnCO$_3$, and Sb$_2$O$_3$. Typically, at 1273K for 20 minutes, 2 h total, compared to the 8-12 h and peak temperature at 1458K in conventional processing. The microwave-synthesized phosphor showed the same phase, morphology, dopant incorporation, and C.I.E. as the control. The brightness of the product was significantly improved when using a shallow tray load of the starting mixture and a pure nitrogen flow during microwave heating.

BAM was synthesized by microwave processing from 1523K to 1773K in the atmosphere of 25% N$_2$ and 75% H$_2$, with fluxed mixtures containing aluminum hydroxide, magnesium oxide, barium carbonate, and europium oxide with a moderate level of BaF$_2$. It was found that 1773K and 20 minutes holding produced white, loose, soft, and fine powders. Compared to the conventional processing that required 1873-1923K for 6-8 h, the microwave processing saved processing time by 75% yet lowered the temperature by 100-150K. Same phase composition was obtained by the microwave processing as by the conventional method.

Both fluxed and unfluxed LAP samples were prepared by microwave processing. The microwave synthesized LAP samples showed excellent properties comparative to the conventional LAP. The microwave synthesized unfluxed LAP showed an exceptionally enhanced thermal stability: there was no significant decrease in brightness up to 673K, and only about 10% decrease at 773K. In contrast, the brightness of conventional control dropped to less than 5% at 673K. In addition, the microwave processing time at peak temperature was <10% of the time required in the conventional process.

Microwave synthesized YOE samples were prepared at times significantly shorter than the conventional synthesis. Both fluxed and unfluxed samples were made.

As shown in Table 1, microwave processing substantially enhanced the reactions and could be conducted at lower temperature than the conventional processing.
Table 1. Comparison between microwave and conventional processing of phosphors

<table>
<thead>
<tr>
<th>Phosphor</th>
<th>Microwave (M)</th>
<th>Conventional (C)</th>
<th>t(M)/t(C)</th>
<th>T(C)–T(M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Halo</td>
<td>20 min, 2h, 1273K</td>
<td>8h, 1473K</td>
<td>1/4</td>
<td>200K</td>
</tr>
<tr>
<td>BAM</td>
<td>20 min, 2h, 1773K</td>
<td>6-8h, 1873-1923K</td>
<td>1/4</td>
<td>150K</td>
</tr>
<tr>
<td>LAP</td>
<td>10 min, 1073K (1293K w/o flux)</td>
<td>4h, 1473K</td>
<td>1/4</td>
<td>400K</td>
</tr>
<tr>
<td>YOE</td>
<td>10 min, 2h, 1473K</td>
<td>7h, 1573K</td>
<td>2/7</td>
<td>100K</td>
</tr>
</tbody>
</table>

Microwave processing of coating

In order to produce an anhydrous silica glass coating, three silica coated zinc silicate samples were microwave treated for 10 minutes at 1173K in a 2.45 GHz microwave furnace while duplicate samples were thermally treated in a conventional electric furnace for the same time and at the same temperature. The processing temperature was chosen to achieve substantial densification of the silica coating without crystallization. As can be seen in Table 2, the luminescence of the microwave processed samples was consistently higher than that of the samples conventionally heated. This implies that microwave processing enhanced viscous sintering of silica gel thus led to a denser, thinner, and more transparent silica coating on the phosphor particles, reducing light scattering and resulted less loss in luminescent emission.

The phosphors coated with silica gel were studied by transmission electron microscopy. Due to the difference in electron transmission between the phosphor particles and the silica coating, the thickness and uniformity of the coating can be identified. The coating was thin, uniform in thickness, and bonded well on the Zn$_2$SiO$_4$. The results indicate that the wetting of silica on the zinc silicate was very good, which led to a good bonding between coating and the phosphor matrix. Secondly, the thickness of the coating was within the range expected from the experimental design, indicating that thickness was controllable. No microcracks were observed on the coating on Zn$_2$SiO$_4$ sample. Compared with the silica-coated zinc silicate that only showed a slight loss in luminescence emission, the coated BAM and CAT phosphors showed over 20% loss. The higher loss in the coated BAM and CAT samples was caused by the microcracks on the coating that increased light scattering.

A few trial experiments were also done to coat the phosphors with alumina gel, but the desired transparent alumina gel has not yet been achieved. The processing conditions for transparent alumina gel are more complicated than those for silica gel. Since alumina sinters at much higher temperatures and crystallizes at much lower temperature than silica, it is difficult to obtain a glassy alumina. Synthesis of alumina gel using an aluminum alkoxide as a precursor might be a solution.

Table 2. Comparison of luminescent emission intensity for thermally heated and microwave treated silica-coated Zn$_2$SiO$_4$ phosphor

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>I$_{525}$ (thermal)</th>
<th>I$_{525}$ (microwave)</th>
</tr>
</thead>
<tbody>
<tr>
<td>uncoated</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Coated 1</td>
<td>0.87</td>
<td>0.92</td>
</tr>
<tr>
<td>Coated 2</td>
<td>0.91</td>
<td>0.97</td>
</tr>
<tr>
<td>Coated 3</td>
<td>0.95</td>
<td>0.98</td>
</tr>
</tbody>
</table>

SEM images show that silica gel wets well on both CAT and BAM. A uniform coating was obtained when the thickness was around 0.1 micrometer. When the coating thickness exceeded 0.3 µm, microcracks formed due to shrinkage of the gels during drying. Measurement of luminescent emission under near UV excitation showed a significant decrease in luminescent intensity with
coating thickness. For example, the CAT emission at 545 nm decreased 30% with 0.1 µm coating. In order to minimize the loss in luminescence, the coating layer should be thin, dense, and uniform. This might be achieved by adjusting the parameters both in the gel preparation and the coating process as well as the sintering.

CONCLUSIONS

Microwave processing can substantially enhance kinetics of the synthesis of phosphors. The study on Halo, BAM, LAP, YOE, showed that, by microwave processing, total processing time in the synthesis of these materials could be reduced by 75%, and the processing temperature could be lowered by 100-400K, depending on the material system. The microwave synthesized unfluxed LAP showed a substantial enhancement in thermal stability, remaining stable up to 773K or so. The substantially reduced processing time and lowered temperature in microwave processing has demonstrated a significant potential for time and energy savings, improvement in the quality of the products, and possibility to produce certain phosphors without using fluxes to reduce contamination and lower the cost in the synthesis of phosphors.

Phosphor materials, P-1, CAT, and BMA, have been coated with silica through a sol-gel approach. Preliminary results show that wetting of silica on both CAT and BMA is fair, and uniform coating is possible. Luminescence emission of the coated CAT and BMA decreased as the coating thickness increased. Coating thicker than 0.3µm led to micro-cracks and debonding during drying. Microwave treatment could improve the interfacial bonding, but optimization of the parameters is required to achieve desired properties.

REFERENCES