Effects of amide types DCCAs on the properties of Y$_2$O$_3$:Eu phosphor powders with spherical shape and fine size

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The effects of amide types drying control chemical additives on the morphologies, BET surface areas, pore sizes, crystal structures, and photoluminescence intensities of the Y$_2$O$_3$:Eu phosphor powders prepared by spray pyrolysis were investigated. The phosphor powders obtained from the spray solutions with N,N-dimethylacetamide (DMA) and N,N-dimethylformamide (DMF) had filled inner structures, low surface areas and high photoluminescence intensities under vacuum ultraviolet illumination. The photoluminescence intensity of the phosphor powders obtained from the spray solution with DMA was 120% of that of the phosphor powders obtained from the spray solution without drying control chemical additive.

Key-words: Spray pyrolysis, Phosphor, Optical material

1. Introduction

Eu-doped Y$_2$O$_3$ powders are used as red-emitting phosphors in flat-panel displays and fluorescent lamps. For practical applications, phosphor powders should have good luminescence properties such as high luminescence efficiency, suitable emission colors, and good screen-printing properties in order to produce phosphor layers with good uniformity, high packing density, and proper adhesion strength onto the substrate. The screen-printing properties depend on many factors such as particle size, particle shape, particle size distribution, and surface properties. In addition, in novel printing processes, such as those involving ink-jet technology, phosphor powders containing small-sized spherical particles with narrow size distributions are very important for achieving good luminescent characteristics.

Spray pyrolysis has been applied to the preparation of multi-component oxide phosphor powders comprising fine spherical particles. The characteristics of the phosphor powders prepared by spray pyrolysis, such as inner structure, size distribution, and powder densification, are affected by the type of spray solution. Various types of organics such as citric acid (CA), ethylene glycol (EG), polyethylene glycol (PEG), and urea were used as additives. The use of spray solutions containing CA and EG or PEG was suggested in large-scale spray pyrolysis for the preparation of the phosphor powders having spherical particles with a filled morphology. The esterification reaction between the carboxyl group in citric acid and the hydroxyl group in ethylene glycol or polyethylene glycol in the spray droplets yields a highly viscous gel consisting of a three-dimensional polymer network. This viscous gel promoted volume precipitation and resulted in the formation of non-aggregated spherical particles with a filled morphology. The effect of N,N-dimethylformamide (DMF), a drying control chemical additive (DCCA), on the characteristics of the phosphor powders prepared by spray pyrolysis was also investigated. The addition of DMF to the polymeric precursor spray solution resulted in an improvement in the morphological characteristics of the phosphor powders. The use of boric acid (H$_3$BO$_3$) flux and a DCCA with the polymeric precursors further improved the photoluminescence (PL) intensity owing to the enhancement of the morphology and crystallinity of the powders. A DCCA is used to control the drying rate of a gel in the sol–gel process. Various types of DCCAs are used to control the morphologies, pore structures, and BET surface areas of the powders or films prepared by the sol–gel process. However, the effects of the type of DCCA on the characteristics of the powders prepared by spray pyrolysis were not investigated.

In this study, amide-type DCCAs were used to control the characteristics of Y$_2$O$_3$:Eu phosphor powders prepared by spray pyrolysis using spray solutions containing polymeric precursors. Formamide (FA), N-methylformamide (MF), N,N-dimethylformamide (DMF), acetamide (AA), and N,N-dimethylacetamide (DMA) were used as the amide-type DCCAs. The effects of these amide-type DCCAs on the morphologies, Brunauer-Emmett-Teller (BET) surface areas, pore sizes, crystal structures, and PL intensities of the Y$_2$O$_3$:Eu phosphor powders were investigated.

2. Experiments

The spray pyrolysis system comprises a droplet generator, a quartz reactor, and a powder collector. A 1.7-MHz ultrasonic spray generator having six vibrators was used to generate a large number of droplets, which were carried into the high-temperature tubular reactor by a carrier gas. The droplets and powders evaporated, decomposed, and/or crystallized in the quartz reactor. The length and diameter of the quartz reactor were 1200 nm and 50 mm, respectively. The spray solutions were prepared by dissolving yttrium nitrate, europium nitrate, CA, EG, and boric acid (H$_3$BO$_3$) flux. The concentrations of CA and EG used as polymeric precursors were 0.2 mol/L each. FA, MF, DMF, AA, and DMA were used as DCCAs to control the drying rate of the droplets inside the hot-wall reactor. The physical properties of the DCCAs are summarized in Table 1. The total concentration of the metal components was 0.5 M. The content of the H$_3$BO$_3$ flux was 1 mass% of the Y$_2$O$_3$:Eu phosphor powders. The concentration of the DCCA was 0.5 M. The flow rate of air used as a carrier...
rrier gas was 10 L/min, and the residence time of the powders inside the reactor was 2.4 s. The as-prepared powders were obtained by spray pyrolysis at 900°C and post-treated at 1100°C for 3 h in a muffle furnace.

The morphological characteristics of the powders were analyzed by scanning electron microscopy (SEM, JEOL, JSM 6060). The crystal structures of the post-treated phosphor powders were investigated by X-ray diffractionometry (XRD, Rigaku DMAX–33) using Cu Kα radiation (λ = 1.5418 × 10⁻² nm). The thermal properties of the precursor powders were measured using a thermo-analyzer (TG-DSC, Netzsch, STA409C) in the temperature range from 40 to 900°C. The surface areas and pore volumes of the powders were measured by the BET method using N₂ gas as the adsorbate. The luminescence characteristics of the prepared powders under vacuum ultraviolet (VUV) illumination were measured using a D₂ lamp.

<table>
<thead>
<tr>
<th>DCCA type</th>
<th>No DCCA</th>
<th>FA</th>
<th>MF</th>
<th>DMF</th>
<th>AA</th>
<th>DMA</th>
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<tr>
<td>Contents</td>
<td>HCONH₂</td>
<td>HCONHCH₃</td>
<td>HCON(CH₃)₂</td>
<td>CH₃CONH₂</td>
<td>CH₃CON(CH₃)₂</td>
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<tr>
<td>Molecular formula</td>
<td>45.04 g/mol</td>
<td>59.07 g/mol</td>
<td>73.09 g/mol</td>
<td>59.07 g/mol</td>
<td>87.12 g/mol</td>
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<tr>
<td>B.P</td>
<td>210°C</td>
<td>198~199°C</td>
<td>153°C</td>
<td>221°C</td>
<td>164.5~166°C</td>
<td></td>
</tr>
<tr>
<td>M.P</td>
<td>2~3°C</td>
<td>-4°C</td>
<td>-61°C</td>
<td>78~80°C</td>
<td>-20°C</td>
<td></td>
</tr>
<tr>
<td>BET surface area</td>
<td>8.67 m²/g</td>
<td>2.98 m²/g</td>
<td>4.34 m²/g</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Mean size</td>
<td>1.4μm</td>
<td>1.20μm</td>
<td>1.12μm</td>
<td>1.11μm</td>
<td>1.14μm</td>
<td>1.12μm</td>
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<tr>
<td>Geometric Standard deviation</td>
<td>1.68</td>
<td>1.63</td>
<td>1.75</td>
<td>1.55</td>
<td>1.58</td>
<td>1.46</td>
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<tr>
<td>BET surface area</td>
<td>3.44 m²/g</td>
<td>2.04 m²/g</td>
<td>1.45 m²/g</td>
<td>2.33 m²/g</td>
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<tr>
<td>Crystallite size</td>
<td>37 nm</td>
<td>34 nm</td>
<td>37 nm</td>
<td>37 nm</td>
<td>37 nm</td>
<td>36 nm</td>
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<td>Relative PL intensity</td>
<td>100</td>
<td>105</td>
<td>110</td>
<td>110</td>
<td>103</td>
<td>120</td>
</tr>
</tbody>
</table>

![Fig. 1. Pore size distribution of the precursor powders.](image)

![Fig. 2. TG/DSC curves of the precursor powders.](image)
3. Results and discussion

The morphologies of the precursor and post-treated phosphor powders obtained by spray pyrolysis from the spray solutions containing different types of DCCAs were investigated from their SEM photographs. All the precursor powders had micron-sized spherically shaped particles, irrespective of the type of DCCA used. However, the internal structures of the precursor powders were dependent on the type of DCCA. The precursor powders obtained from the spray solutions containing FA, MF, and AA had hollow and porous internal structures. On the other hand, the precursor powders obtained from the spray solutions containing DMF and DMA had filled internal structures. Figure 1 shows the pore volumes of the precursor powders measured by the BET method. The precursor powders obtained from the spray solution without the DCCA had mesopores (2–10 nm) and macropores (>10 nm). However, the addition of a DCCA to the spray solution decreased the macropore volume. The precursor powders obtained from the spray solution containing DMA had larger mesopore volumes than those obtained from the spray solution containing AA. On the other hand, the precursor powders obtained from the spray solution containing AA had larger macropore volumes (pore diameters: >20 nm) than those obtained from the spray solution containing DMA. The BET surface areas of the precursor powders obtained using the spray solutions containing DMA and AA were 4.34 m²/g and 2.98 m²/g, respectively. On the other hand, the BET surface area of the precursor powders obtained from the spray solution without any DCCA was 8.67 m²/g. The mean particle sizes and geometric standard deviation of the precursor powders obtained by spray

![SEM photographs of the post-treated Y₂O₃:Eu phosphor powders.](image-url)
pyrolysis using spray solutions containing various DCCAs are shown in Table 1. In order to minimize errors, the mean particle sizes of the powders were determined from their SEM photographs by counting more than 500 particles in each sample. The precursor powders had similar mean particle sizes and particle size distributions, irrespective of the DCCA type. The mean particle sizes of the phosphor powders obtained from the spray solution containing DMF and DMA were 1.11 μm and 1.12 μm, respectively. On the other hand, the mean particle size of the phosphor powder obtained from the polymeric precursors spray solution without any DCCA was 1.4 μm. The addition of the DCCA to the spray solution decreased the mean sizes, BET surface areas, and geometric standard deviation of the precursor powders. The thermal properties of the precursor powders prepared by spray pyrolysis using the spray solutions containing FA and DMA are shown in Fig. 2. The total weight losses of the precursor powders obtained from the spray solutions containing FA and DMA were 7.6 and 23.1 mass%, respectively. The exothermic peaks in the DSC curves confirmed the decomposition of the residual carbon component. The precursor powders obtained from the spray solution containing FA yielded a single exothermic peak at 605.8°C. On the other hand, the precursor powders obtained from the spray solution containing DMA yielded multiple exothermic peaks at 469.9°C, 543.3°C, and 684.7°C. The differences in the thermal properties of the powders were due to the different morphologies of the precursor powders, which in turn depended on the type of DCCA added to the spray solutions. In spray pyrolysis, no marked decomposition of the carbon component was observed in the precursor powders having dense internal structures.

![High magnification SEM photographs of the post-treated Y₂O₃:Eu phosphor powders.](image-url)

**Fig. 4.** High magnification SEM photographs of the post-treated Y₂O₃:Eu phosphor powders.
Figures 3 and 4 show the SEM photographs of the post-treated Y$_2$O$_3$:Eu phosphor powders. The phosphor powders retained the micron-sized spherical-shaped particles of the precursor powders even after the post-treatment. However, the difference in the morphologies of the precursor powders affected the morphologies, mean particle sizes, and particle size distributions of the phosphor powders, as shown in Fig. 4. The phosphor powders obtained from the spray solutions containing DMA and DMF had dense morphologies and fine particles. On the other hand, the phosphor powders obtained from the spray solutions containing FA, MA, and AA had hollow and porous morphologies. The BET surface areas of the phosphor powders obtained from the spray solutions containing DMA and DMF were 1.41 m$^2$/g and 1.45 m$^2$/g, respectively. On the other hand, the BET surface areas of the phosphor powders obtained from the spray solutions containing FA, MF, and AA were 3.44, 2.04, and 2.33 m$^2$/g, respectively. Depending on the DCCA type, the mean crystallite sizes of the powders measured by Scherrer’s equation varied from 34 to 37 nm. Figure 5 shows the XRD patterns of the post-treated Y$_2$O$_3$:Eu phosphor powders. The phosphor powders had cubic crystal structures, irrespective of the type of DCCA used. The mean crystallite sizes of the phosphor powders calculated using Scherrer’s equation were similar, as described in Fig. 5. Figure 6 shows the PL spectra of the phosphor powders obtained from the spray solutions containing various types of DCAs. The phosphor powder obtained from the spray solution containing DMA had the highest PL intensity under VUV illumination. The PL intensity of the phosphor powder obtained from the spray solution without any DCA. The PL intensities of the phosphor powders prepared in this study were also compared with those of the commercial Y$_2$O$_3$:Eu phosphor powders prepared by the solid-state reaction method. The PL intensity of the phosphor powder obtained from the spray solution containing DMA was 95% that of the commercial product.

4. Conclusions

Amide-type DCAs such as FA, MF, DMF, AA, and DMA were used to control the characteristics of Y$_2$O$_3$:Eu phosphor powders prepared by spray pyrolysis. DMA and DMF were efficient as DCAs when added to the spray solution, and yielded Y$_2$O$_3$:Eu fine phosphor powders with spherical particles, low surface areas, and high PL intensities.

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Reference