Preparation of Ce-doped yttrium aluminum garnet phosphor particles using spray drying method

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**ABSTRACT**

The potential phosphor particles of Ce-doped yttrium aluminum garnet (YAG: Ce) particles were prepared using the spray drying method. This method yields a homogenous composition, regularly shaped particles, and has a short processing time. Meanwhile, acid catalysts affect the yield and particle shape of the spray dried particles. Therefore, in this study, three common acids i.e. formic acid, oxalic acid, and citric acid, were used to prepare the YAG:Ce powders. The X-ray diffraction measurements showed that all acid catalysts formed a single YAG phase. The SEM surface images and FIB cross-sectional images revealed two typical smooth hollow spherical and concave solid spherical geometries. The statistical analysis showed that the particle size followed the order of citric acid-treated powder > oxalic acid-treated powder > formic acid-treated powder. Meanwhile, the citric acid-treated phosphor had a higher photoluminescence (PL) intensity than the formic acid- and oxalic acid-treated phosphors. The PL intensities of these three phosphors were correlated with their crystalite sizes, which is affected by the heat of combustion of the acid catalysts. Furthermore, the influence of the precursor properties on the corresponding formation mechanisms of the YAG:Ce powders was discussed.

1. Introduction

White light-emitting diodes (LEDs) have received considerable attention owing to their high energy conversion efficiency and low cost [1,2]. They can potentially replace high energy consuming conventional incandescent and fluorescent lamps and also save energy. Although various color phosphors have been studied, the most popular yellow phosphor is the Ce-doped yttrium aluminum garnet (Y\textsubscript{2}Al\textsubscript{5}O\textsubscript{12}: Ce; YAG: Ce), which combines with a blue light-emitting chip (e.g. GaN and InGaN) to form white LEDs [3]. This is because YAG: Ce has an intense broad yellow emission band that tolerates residual blue to produce white light [4]. Although YAG:Ce has been known as a phosphor for many years, and has also been commercially used in various industrial applications, such as headlights for cars, studies on the quantum yield of the YAG: Ce phosphors are still elusive. Thus, spray-dried YAG: Ce phosphors must be developed to compare them with other materials and further enhance their prospects as promising candidates.

Many methods are used to produce YAG: Ce phosphor powders, for example, the solid-state method [1,2], sol-gel method [5], microwave-assisted method [6], and spray drying (SD) [7]. Although the solid-state and sol-gel methods are the most popular, they have some disadvantages that need to be addressed. First, the solid-state method requires high reaction temperatures (>1600°C) [1] (this results in high costs), and yields irregular morphology and poor homogeneity [2] which may affect the photoluminescence (PL) properties of the phosphor powders [7]. Although the sol-gel method achieves morphological control and homogeneity, it requires a long fabrication time [8]. In contrast, the SD method yields homogenous particles with a regular shape and has a shorter preparation time compared to the solid-state and sol-gel methods [7,9]. Therefore, in this study, we prepared YAG: Ce powders using the SD method.

In the SD method, the acid catalysts affect the yield, particle shape, and particle size [7]. To the best of our knowledge, no studies have reported the correlation between the acid catalysts and PL properties. Therefore, in this study, three common acids i.e. formic acid, oxalic acid, and citric acid were used to prepare YAG: Ce phosphor powders using the SD method. The phase composition, morphology, and PL properties of the three acid-treated phosphor powders were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), nitrogen adsorption/desorption (Brunauer-Emmett-Teller (BET) method), and fluorescence spectrometry, respectively. In addition, the
correlation between the morphology, crystallite size, and PL properties of the spray-dried YAG: Ce powders was discussed.

2. Materials and methods

2.1. Synthesis

YAG: Ce phosphor powders were synthesized from three distinct acid treatments using the SD method. Firstly, 47.74 g yttrium nitrate hexahydrate (Y(NO₃)₃·6H₂O, 99.8 wt%, Aldrich, St. Louis, USA), 78.98 g aluminum nitrate nonahydrate (Al(NO₃)₃·9H₂O, 98 wt%, Showa, Tokyo, Japan), and 0.46 g ceric ammonium nitrate ((NH₄)₂Ce(NO₃)₆, 98.5 wt%, J.T. Baker, Philadelphia, USA) were dissolved in 250 g ethanol and stirred at 25°C for 1 h. Afterward, these three YAG: Ce precursor solutions were mixed with 1 M formic acid (CH₂O₂, 98 wt%, Aldrich, Darmstadt, Germany), oxalic acid (C₂H₂O₄, 99 wt%, Aldrich, Darmstadt, Germany), or citric acid (C₆H₈O₇, 99.5 wt%, Showa, Tokyo, Japan) modifiers, and stirred at room temperature (25 ± 1°C) for 1 h. These precursor solutions were injected into the chamber of a spray dryer system (SD D0-03, IDTA, New Taipei, Taiwan) and dried at 200°C. The spray-dried powders were collected by a cyclone collector. Then, these three powders were calcined in air at 1400°C for 3 h.

2.2. Characterization

Initially, the phase compositions and crystallite sizes of the phosphor powders were determined by X-ray powder diffraction (D2 Phaser, Bruker, Karlsruhe, Germany) using a Cu Kα source (λ = 1.54 Å) with an operating voltage of 30 kV and a current of 10 mA. The measurement was taken at a diffraction angle (2θ) ranging from 20° to 80°, step size of 0.05°, and detection time of 0.5 s per step. From the XRD diffraction results, the crystallite sizes were calculated using the Scherrer equation

\[
\tau = \frac{0.9\lambda}{\beta \cos \theta}
\]

where \( \tau \) is the average size of the coherently diffracting domains, which corresponds to the crystallite size, \( \lambda \) is the X-ray wavelength, \( \beta \) is the peak broadening at full width half maximum (FWHM), and \( \theta \) is the diffraction angle.

Then, the surface morphologies, inner morphologies, and particle size distributions of the three powders were analyzed using a scanning electron microscope (SEM) equipped with a focused ion beam (Quanta 3D FEG, FEI, USA). Besides determining the surface morphologies, this equipment was also used to cut the phosphor powders using a germanium ion beam at a sample tilted angle of 52° to characterize the inner morphologies. For each specimen, more than five cross-sectional particles were prepared to observe their inner structures. To obtain reliable particle size distributions, the ImageJ image processing program was used to count more than 300 particles of each sample. In addition, the specific surface area values for the three acid-treated powders were determined using the BET method (Tristar, Micromeritics, Norcross, GA). Each powder was degassed at 150°C for 3 h and then measured at −196°C.

Subsequently, a fluorescent spectrometer (FP-8500, JASCO, Tokyo, Japan) with a 150 W Xe lamp was used as the excitation light source to record the excitation spectra of the YAG: Ce powders and analyze their PL properties at room temperature. The PL spectra were determined at an excitation wavelength of 530 nm. The accuracy of the quantum yield measurement depends on various factors, such as the sample quantity, excitation power density, temperature of the sample arising from the high-power density excitation, and reflectivity of the sample holder. To measure the quantum yield of the emission bands, an equal 0.2 g weight of each phosphor was packed tightly inside a specially designed powder sample holder, which had a glass window for excitation and emission. The holder was placed in the sample port of the integrated sphere and excited with 450 nm blue light from the 150 W Xe lamp. The emission spectra were collected in the 480–640-nm range for all the phosphor specimens. In addition, the data of quantum yield and the optical absorbance of commercial YAG powder (GNYAG3635-01-11, Internatix Co. Ltd, Suzhou China) were obtained as the reference.

3. Results

3.1. Phase composition and morphology

Figure 1 shows the X-ray diffraction patterns of the formic acid, oxalic acid, and citric acid-treated powders. First, the XRD pattern of the formic acid-treated phosphor powder reveals the single crystalline phase of the YAG (JCPDF number of 33–0040). This phase contains eighteen diffraction peaks in the range of 2θ from 20° to 80°. Similar XRD patterns were also observed for the oxalic-treated and citric acid-treated powders. Based on the Scherrer equation, the FWHM values of the phosphor powders were 0.0073 ± 0.0003, 0.0051 ± 0.0002, and 0.0039 ± 0.0001; these yielded average crystallite sizes of 23 ± 1, 33 ± 1, and 43 ± 1 nm for the formic acid, oxalic acid, and citric acid-treated phosphor powders, respectively. Therefore, the XRD results suggest that (i) the three acid-treated YAG: Ce powders were successfully synthesized using the SD method, and (ii) the citric-acid-treated powder exhibited a larger crystallite size (43 nm) than the oxalic acid (33 nm) and formic acid-treated (23 nm) YAG: Ce powders.

The surface and inner morphologies of the formic acid, oxalic acid, and citric acid-treated YAG: Ce powders were characterized using FIB-SEM, as shown in
**Figure 1.** XRD patterns of formic acid, oxalic acid, and citric acid-treated YAG:Ce powders calcined at 1400°C for 3 h in air.

| Two theta (°) | Formic acid-treated phosphor | Oxalic acid-treated phosphor | Citric acid-treated phosphor |
|--------------|-------------------------------|-----------------------------|-----------------------------|
| (220)        |                               |                             | Y\textsubscript{3}Al\textsubscript{5}O\textsubscript{12} (PDF 33-0040) |
| (412)        |                               |                             |                             |
| (421)        |                               |                             |                             |
| (532)        |                               |                             |                             |

**Figure 2.** The SEM images suggest that there are two typical smooth and concaved spherical morphologies. The spherical particles were formed in the formic acid-treated powder, while the concaved spherical particles were found in the oxalic acid and citric acid-treated powders. Meanwhile, more than five cross-sectional particles were prepared for each specimen. The results show that the formic acid-treated powder had entirely hollow particles, whereas the oxalic acid and citric acid-treated powders had entirely solid particles. Therefore, these SEM images and the corresponding cross-sectional images (**Figure 2**) reveal that two
distinct morphologies exist i.e. the smooth hollow spheres (for the formic acid-treated YAG: Ce powder) and concaved solid spheres (for the oxalic acid and citric acid-treated YAG: Ce powders).

### 3.2. Particle size distribution and specific surface area

Figure 3 shows the statistical analysis of the particle sizes of all acid-treated YAG powders. The average particle sizes and standard deviations of the formic acid, oxalic acid, and citric acid-treated powders were 4.0 ± 1.5, 6.6 ± 3.1, and 7.6 ± 3.6 μm, respectively. The data suggest that the particle size follows the order: citric acid-treated powder > oxalic acid-treated powder > formic acid-treated powder. In addition, the BET data showed that the specific surface areas of the YAG: Ce powders treated with formic acid, oxalic acid, and citric acid were 16.2 ± 11.2, 16.7 ± 9.4, and 63.2 ± 5.4 m²/g, respectively. The citric-treated powder exhibited the highest specific surface area. This supports the results of morphological analysis which state that the concaved porous spherical particles have a larger specific surface area (63.2 ± 5.4 m²/g) than the concaved solid spherical particles (16.2 ± 11.2 m²/g) and smoother hollow spherical particles (16.7 ± 9.4 m²/g).

![Graphical representation of particle size distribution](image)

#### Figure 3.

Particle size histograms of (a) formic acid, (b) oxalic acid, and (c) citric acid-treated YAG:Ce powders calcined at 1400°C for 3 h in air.

### 3.3. PL intensity and external quantum efficiency

Figure 4(a) shows the detailed emission spectra of the three acid-treated YAG phosphor powders measured in the wavelength range of 480–640 nm by monitoring the emission at 450 nm. These spectra show that all acid-treated powders have an intense band at 530 nm (5d→4 f). Additionally, the PL excitation properties of the acid-treated YAG phosphor powders were examined using the PL emission spectra at 530 nm, and the results are shown in Figure 4(b). Based on the PL emission and excitation spectra, the main emission can be found at 530 nm, which corresponds to the direct excitation of 5d→2F₅/₂ and 5d→2F₇/₂ shell transitions. Moreover, the citric acid-treated powder emitted the highest intensity compared to the oxalic acid-treated and formic acid-treated powders (168, 152, and 147 counts for the citric acid-treated powder, oxalic acid-treated powder, and formic acid-treated powder, respectively). In addition, the internal quantum efficiencies of the YAG: Ce powders treated with formic acid, oxalic acid, and citric acid were 68.55, 73.13, and 75.02% under the corresponding optical absorbances of 53.17, 47.99 and 53.14%, respectively (compared to the internal quantum efficiency of 95.75% and optical absorbance of 81.74% for the commercial YAG powder). In addition, the internal
quantum efficiency also followed the same trend as the PL intensity, with citric-treated powder exhibiting the highest external quantum efficiency.

4. Discussion

The morphological analysis of these spray-dried YAG:Ce phosphor powders shows that all particles are spherical in shape, as shown in Figure 2. Typically, spherical shaped particles are generated by the “droplet to particle conversion” spray dried mechanism [10]. This mechanism removes the solvent from the droplets produced by the atomizer and transform them into particles. This is similar to the spray pyrolysis (SP) “one-particle-per droplet” mechanism [11]. Meanwhile, the SEM results suggest that the citric acid-treated powder had a rougher surface (more concaves on the surface) than the oxalic acid and formic acid-treated powders. This could be explained as follows: Carbon dioxide and water vapor are released during the combustion of carboxylic acids, and these gases create the concaves on the particle surfaces during the SP calcination step [12,13]. Citric acid contains more carboxylic groups than oxalic acid and formic acid (three, two, and one carboxylic functional groups for citric acid, oxalic acid, and formic acid, respectively). Therefore, more gases, which create more concaves, are formed from citric acid than from oxalic acid and formic acid. Meanwhile, the FIB-prepared cross-sectional results indicate that the formic acid-treated powder had a hollow inner structure, whereas the oxalic acid and citric acid-treated powders had solid structures. This was because of the solvent evaporation rate during the SP process [10]. Since the boiling point of formic acid
Figure 5. The PL intensity as the function of (a) specific surface area and (b) average crystallite size for the YAG:Ce powders.

(101°C [14]) is lower than that of the oxalic acid (365°C [15]) and citric acid (310°C [16]), the formic acid solvent has a higher evaporation rate than that of the oxalic acid and citric acid solvents. Therefore, during the spray drying process, the precursor solutes precipitate earlier on the droplet surface and trap the remaining solvent in the center of the particle. This results in “surface precipitation” hence the hollow structure [11]. In contrast, owing to the high boiling points of oxalic acid and citric acid, the solvent and precursor solutes precipitate simultaneously throughout the whole droplet. Therefore, these undergo “volume precipitation” and form particles with a solid structure [11].

The order of the crystallite size (citric acid-treated powder > oxalic acid-treated powder > formic acid-treated powder) is discussed below. Based on the previous studies, the factors that might influence the crystallinity of the spray pyrolyzed particles are the precursor types [17], precursor concentration [18], and synthesis temperature [19]. However, in this study, the precursor concentration and synthesis temperature were maintained for all samples; therefore, the only variable was the acid precursor type. In the
precursor solution, the cations of Y, Al, and Ce were completely mixed in the nitrate solution [20], and these ions were chelated by formic acid, oxalate acid, and citric acid, respectively. To noted, the formic acid, oxalate acid, and citric acid contained one, two, and three carboxyl groups and are able to form dentate, bidentate, and tridentate, respectively. According to Wang et al. [21], the stability of tridentate is better than bidentate and monodentate due to the better chelation formation for the stable metal complexes, which promote the crystal growth [22]. Therefore, the citric acid-treated powder had the largest crystallite among the three spray-dried YAG: Ce phosphor powders.

Finally, Figure 5(a,b) show the correlation between the PL intensity and the specific surface area and crystallite size of the acid-treated YAG phosphor powders. Figure 5(a), shows the PL intensity as a function of the specific surface area for all specimens. Previous studies have reported that a larger surface roughness improves the PL intensity, consequently, the surface approaches an ideal diffusely reflecting surface, which is known as the Lambertian surface [23,24]. However, the results showed that the YAG: Ce specimens treated with formic and oxalic acids had similar specific surface areas of 16 m²/g, yet their PL intensities differed by approximately 4%. Meanwhile, the YAG: Ce treated with citric acids had approximately four times the specific surface area at 63 m²/g. This resulted in an increased PL intensity of approximately 29%. These results indicate that the specific surface area does not influence the PL intensity significantly. Meanwhile, the correlation between the PL intensity and crystallite size is shown in Figure 5(b). It can be observed that the PL intensity is linearly correlated with the crystallite size, indicating that the crystallite size is the dominant factor affecting the PL intensity. This is possibly attributed to the smaller amount of defects in the phosphor of higher crystallinity for the citric acid-treated powder, which facilitates electron translation. These defects favor energy transfer through the non-radiative pathway, named the photoluminescence quenching effect [25–27]. Therefore, the citric acid-treated YAG:Ce powder with the highest crystallinity exhibits the highest PL intensity compared to the formic acid and oxalate acid-treated YAG:Ce powders.

5. Conclusion

In this study, YAG: Ce powders treated with various acids were prepared using the spray drying method. The characterization of the phase composition and photoluminescence confirmed the successful synthesis of the phosphor powders. In addition, the morphologies of the particles were revealed by SEM images. Meanwhile, the formation mechanism of the FIB prepared cross-sectional specimens was discussed. Finally, the photoluminescence measurements showed a linear relationship between the crystallite size and PL intensity. This indicates that the specimen with a larger crystallite size exhibits stronger PL intensity. Therefore, we demonstrated that the YAG: Ce powder treated with citric acid can be considered as a potential phosphor candidate.

Acknowledgments

The authors acknowledge the financial support from the Tokushima University, Japan; National Taiwan University of Science and Technology, Taiwan (Grant Numbers of TU-NTUST-107-03); and Ministry of Science and Technology of Taiwan (MOST 106-2221-E-011-049 and 108-2923-E-011-007-MY3).

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by the Ministry of Science and Technology of Taiwan [MOST 106-2221-E-011-049]; Tokushima University, Japan; National Taiwan University of Science and Technology, Taiwan [TU-NTUST-107-03]; Ministry of Science and Technology of Taiwan [MOST 108-2923-E-011-007-MY3].

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