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Engineering phosphors for improved brightness

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Factors affecting the cathodoluminescent (CL) efficiency of phosphors include: morphology, size, stoichiometry, composition, and surface of the phosphors. In the design of phosphors for low-voltage operations, processes such as surface etching are used to enhance phosphor efficiency. In this study, zinc-activated ZnO phosphors were subjected to three processes: acid etching, ball milling, and/or ultrasonic vibration, and the effect of each process on the CL efficiency studied. It is found that the brightness of phosphors increases 40% after ultrasonic vibration followed by etching twice with 0.005 M HNO_3.

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1. Introduction

Field emission displays (FED) have been actively investigated for the development of the full-color flat panel display in recent years. In the development of FED, it is important to develop phosphors with sufficient luminant efficiency at low voltages (< 1 kV). Zinc oxide phosphors have recently gained much attention because of their potential use in low-voltage fluorescence applications, such as FEDs [1, 2]. One major obstacle in the application of FEDs is the non-emissive layer of material that exists on the surface of the phosphors. The non-emissive layers are attributed to the non-radiative surface effects such as defects, contamination, or band bending [3]. Because the voltage used in FEDs is low, the penetration of the electrons into the phosphor particle is relatively shallow. The low penetration of electrons into the particle means that emission observed from the phosphor must involve energy transfer within the surface layer. Hence, a low luminescent efficiency is observed at low voltages due to the loss of energy to non-radiative centers within the non-emissive surface. It is clear that, at low voltages, the nature and perfection of the surface of the phosphors play an important role in the performance of FED phosphors. Previous work reports an increase in cathodoluminescent intensity of ZnO : Zn phosphors etched with a basic aqueous solution of sodium borohydride [3]. It is argued that the enhanced efficiency of the phosphor particles may be attributed to a change in surface structure or an increase in the surface coverage of luminescent centers induced by the reductive etch. However, the root causes for the increase of efficiency are not understood yet.

In the design of phosphors for low-voltage operation there are three important factors to be considered: (1) the morphology and size; (2) the stoichiometry and composition; and (3) the surface of the phosphors [4]. This is ongoing research. In our previous work, the effect of the stoichiometry and composition on the cathodoluminescent properties of ZnO : Zn phosphor were investigated [5, 6]. In this study, several treatment methods, including ball milling, ultrasonic vibration, and acid etching, have been applied to ZnO : Zn phosphor powders. The effects of various treatments on the luminescence of phosphors are investigated. The possible mechanisms are explored. The phosphor employed in this study is zinc-activated zinc oxide prepared by solid-state sintering of 95 wt %ZnO–5 wt %ZnS in a N_2 atmosphere [5, 6].

2. Experimental procedures

Zinc-doped zinc oxide phosphors were prepared by solid-state sintering of mixtures of ZnO and ZnS powders in a N_2 atmosphere. Details of phosphor preparation and characterization were reported elsewhere [5, 6]. Three different processes were applied to the as-sintered phosphors, they are: ball milling, ultrasonic separation, and acid etching. The ball-milling process was carried out in a ceramic jar at a speed of 250 r.p.m. for 2 h. In the ultrasonic separating experiment, the as-sintered phosphor powders were placed in a glass beaker with deionized (DI) water and stirred with air bubbles. The glass beaker was placed in an ultrasonic wave generator and shaken for 10 min. After the ultrasonic shaking, the powders were then dried in an oven. For the acid etching experiments, hydrochloric acid and/or nitric acid with various concentrations were employed. The etches were performed at a slurry concentration of 250 ml acid solution per gram ZnO : Zn powder. The powders were stirred in the acid for 3 min; then rinsed in DI water twice for two minutes each. For the two-step etching, this process was repeated twice. The slurry was decanted, and the resultant powder was rinsed with water and then baked in an oven at 120 °C for 3 h.

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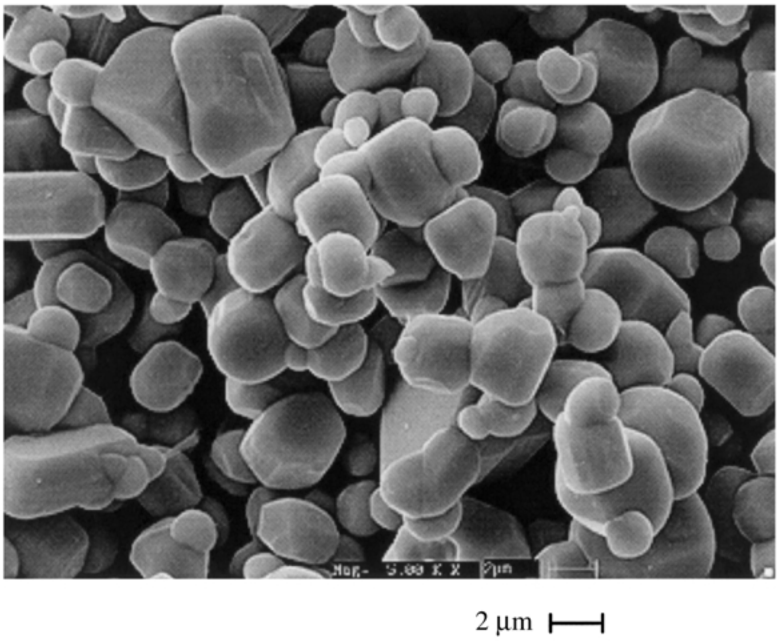

Figure 1 SEM images of the as-sintered phosphor powders.

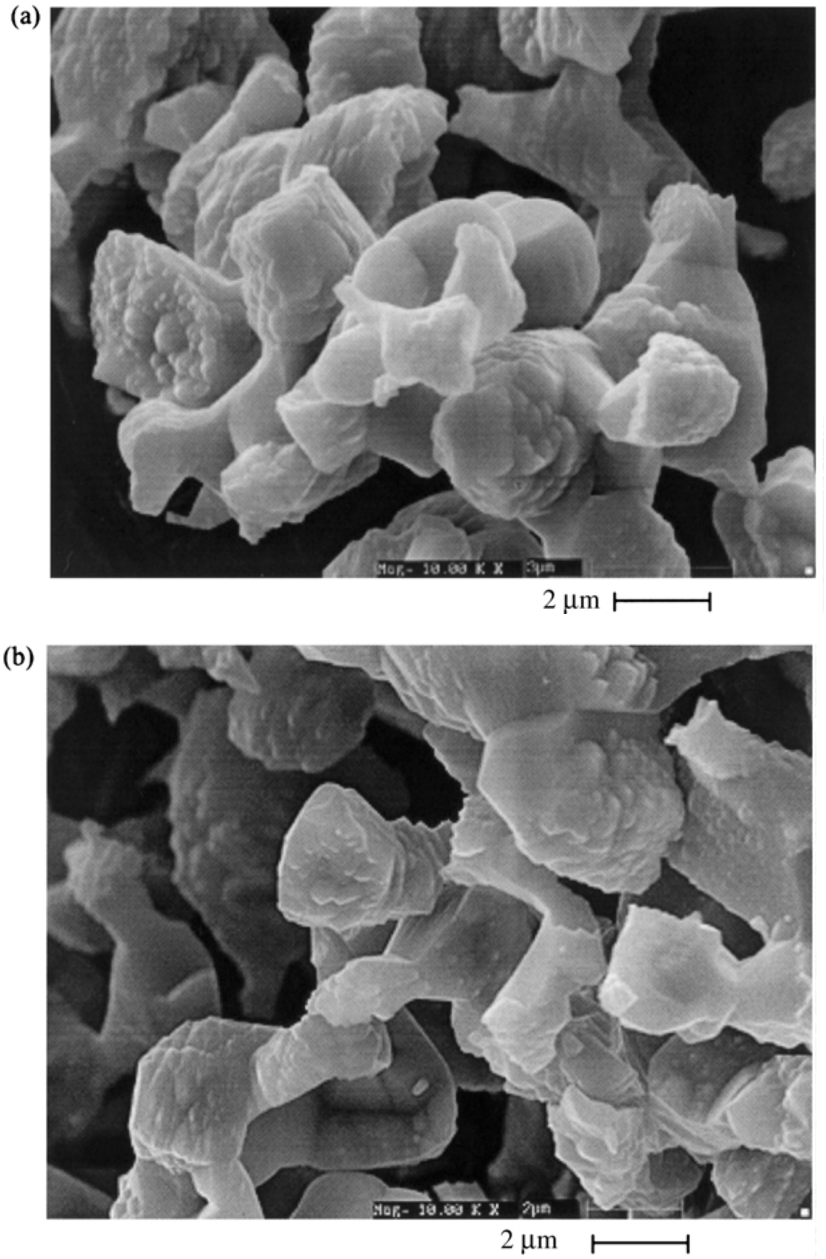

Figure 2 SEM images of the phosphor powders etched with: (a) 0.05 M; (b) 0.03 M; (c) 0.01 M; and (d) 0.005 M HCl.

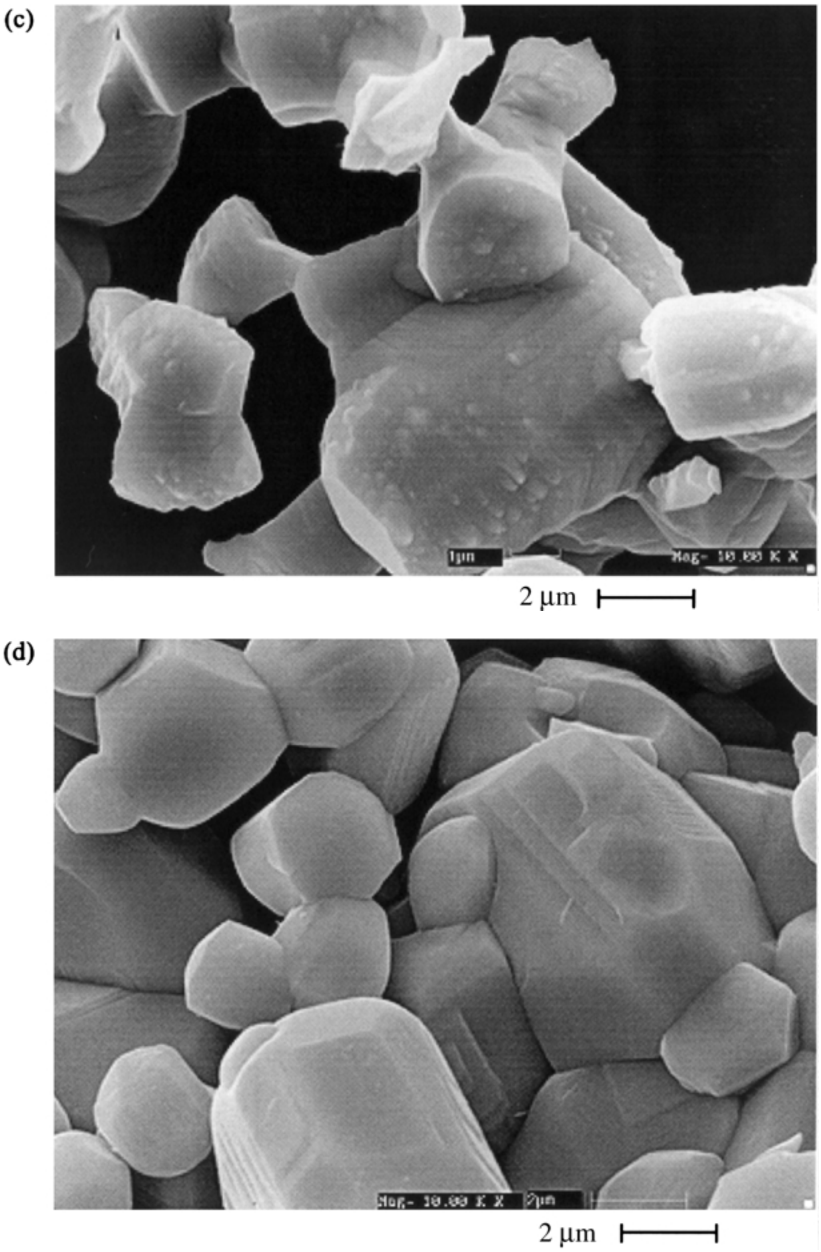

Figure 2 (Continued)

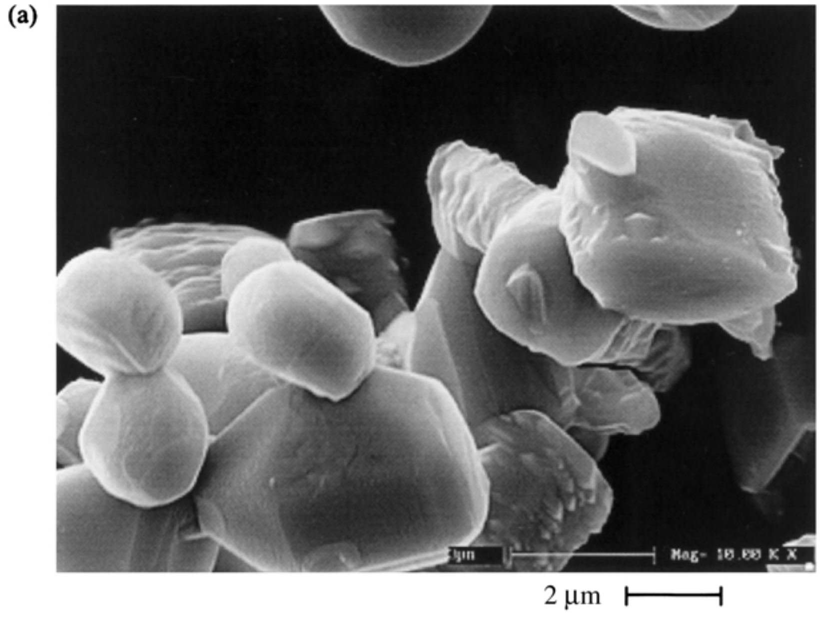

Figure 3 SEM images of the phosphor powders etched with: (a) 0.05 M; (b) 0.03 M; (c) 0.01 M; and (d) 0.005 M HNO_3.

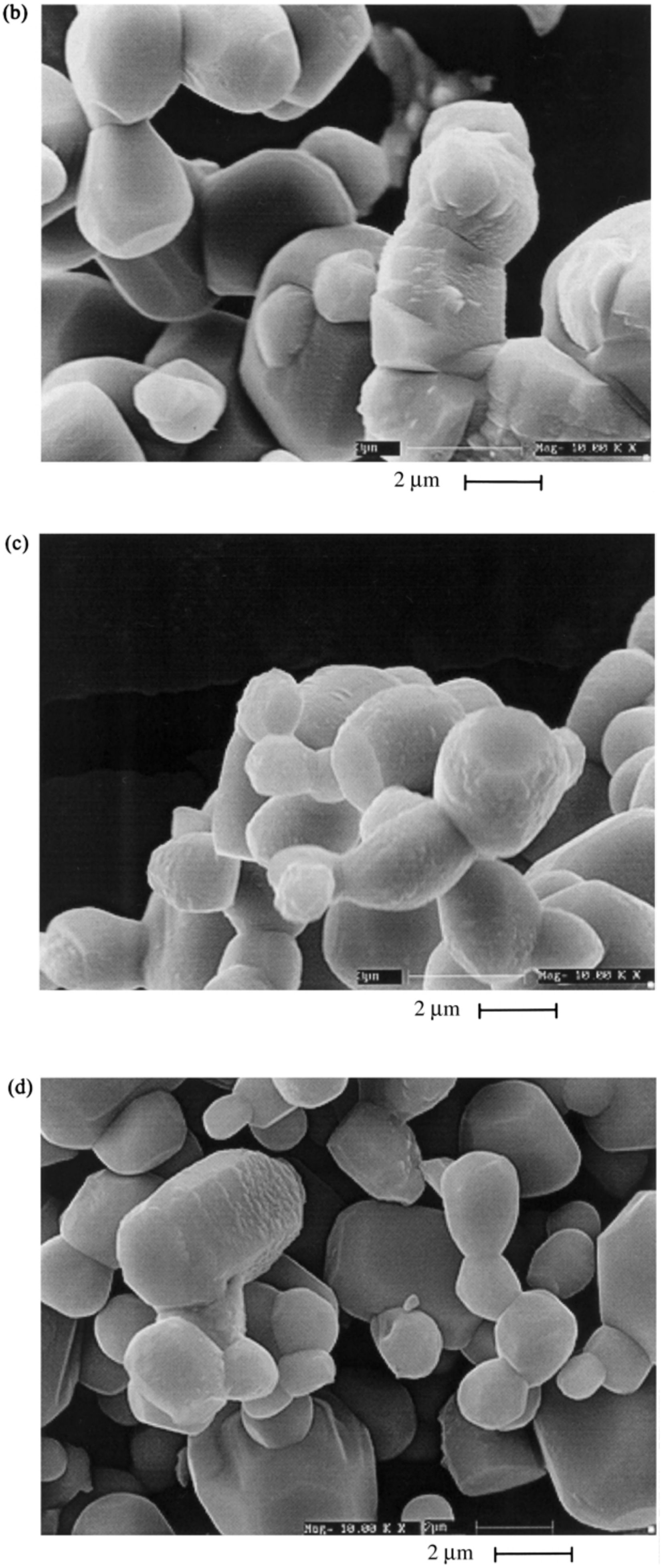

Figure 3 (Continued)

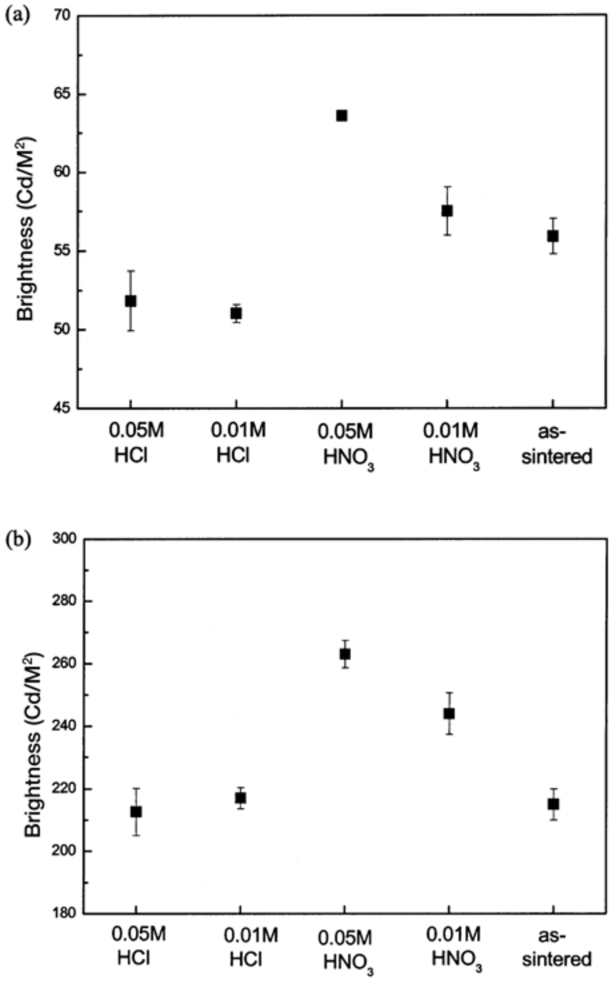

Figure 4 Brightness of the phosphors before and after etching, measured at: (a) 1 μA, 800 V and (b) 5 μA, 800 V.

The as-treated phosphor powders were examined with a scanning electron microscope (SEM, Leica S440, Japan) to investigate the particle size, particle shape, and surface morphology. The phosphor powder was further examined with a laser particle sizer (analysette 22, Fritsch) to evaluate the particle-size distribution. Details of sample preparation, powder analysis, and luminescence measurement were reported elsewhere [5, 6].

3. Results and discussion

Figs. 1–3 are the scanning electron microscopy (SEM) photographs of the as-sintered phosphor and phosphor powders etched with HCl and HNO_3, respectively. As observed from the SEM photos, phosphor powders etched with HCl have a rougher surface than those etched with HNO_3, and the higher the acid concentration, the rougher the powder surface. The ideal morphology of powder phosphor is that of a perfect sphere. However, powders etched with HCl show irregular shapes. Fig. 4 gives the brightness of the phosphor before and after etching. The brightness of the sample etched with HCl decrease while those etched with HNO_3 increase 5–15% at 1 μA, 800 V and 20–30% at 5 μA, 800 V. The decrease in brightness may be due to the rough surface and irregular shapes of HCl-etched powders.

The weight loss of phosphor after etching is summarized in Table I. Although HNO_3 etching removes the non-emissive layer on the surface and enhances the brightness of the phosphor, the weight loss of the sample etched with a concentration larger than 0.01 M is too high to be practical. Hence, a multi-step etching process with low concentration acid is employed. As indicated in Fig. 5, the brightness of the phosphor etched with 0.005 M HNO_3 twice increases ∼ 10% at 1 μA, 800 V and 25% at 5 μA, 800 V as compared to the as-sintered ones.

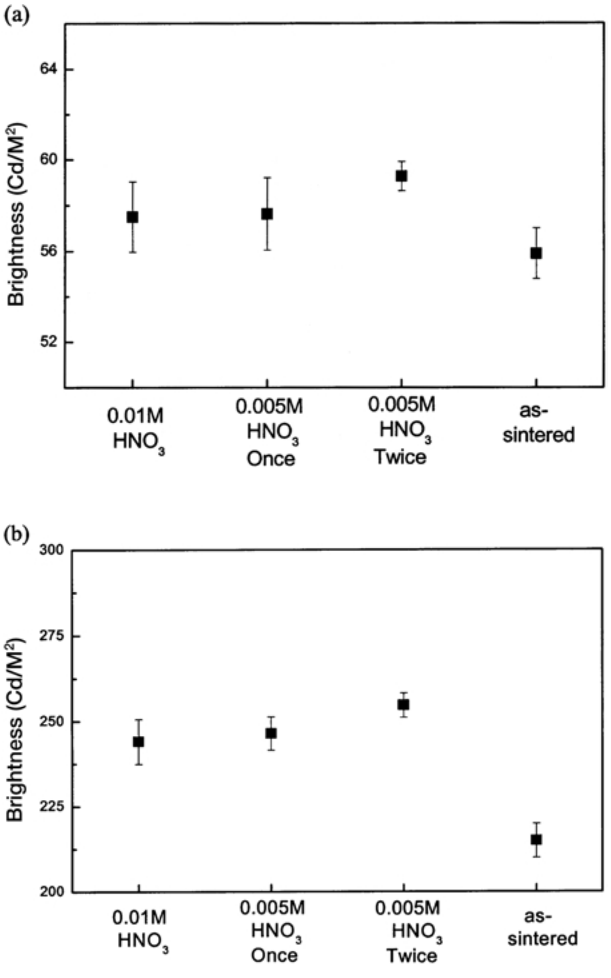

Figure 5 Brightness of phosphors with one or two-step etching, measured at (a) 1 μA, 800 V and (b) 5 μA, 800 V.

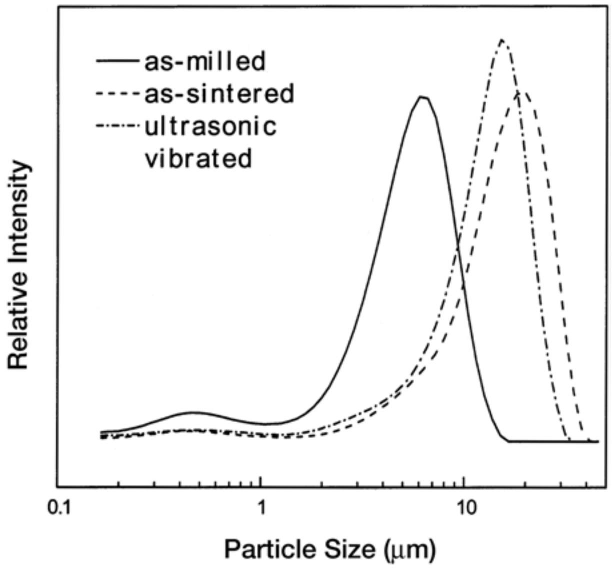

Figure 6 Particle-size distribution of the as-sintered, as-milled, and ultrasonic-vibrated phosphors.

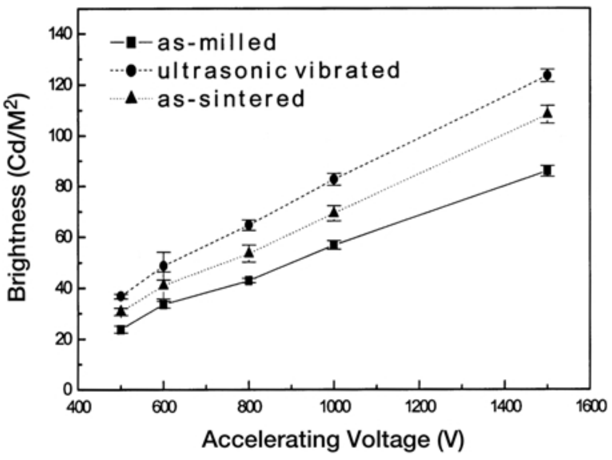

Figure 7 Brightness versus accelerating voltage for the as-sintered, as-milled, and ultrasonic-vibrated phosphors.

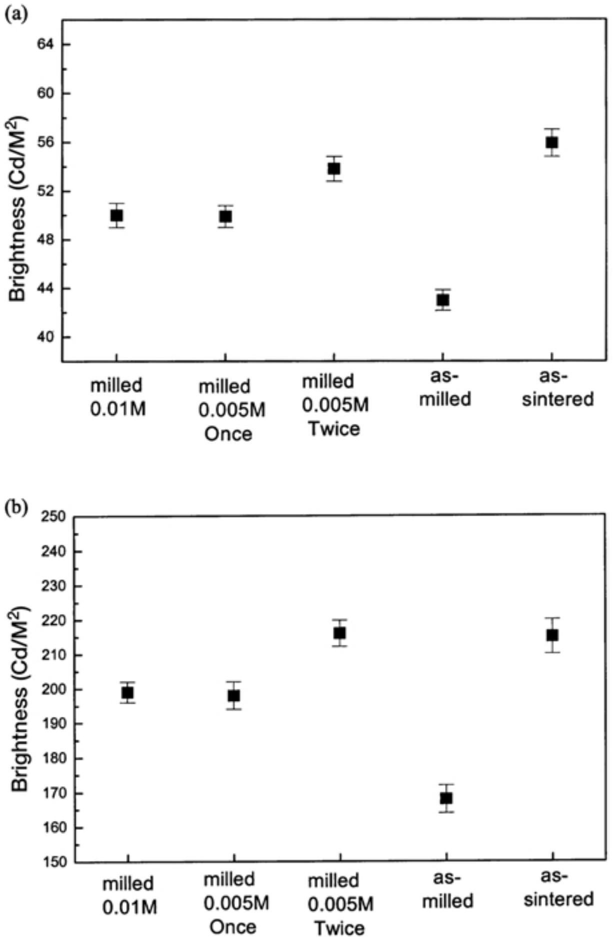

Figure 8 Brightness of milled phosphors with one or two-step HNO_3 (0.01 M or 0.05 M) etching measured at; (a) 1 μA, 800 V and (b) 5 μA, 800 V.

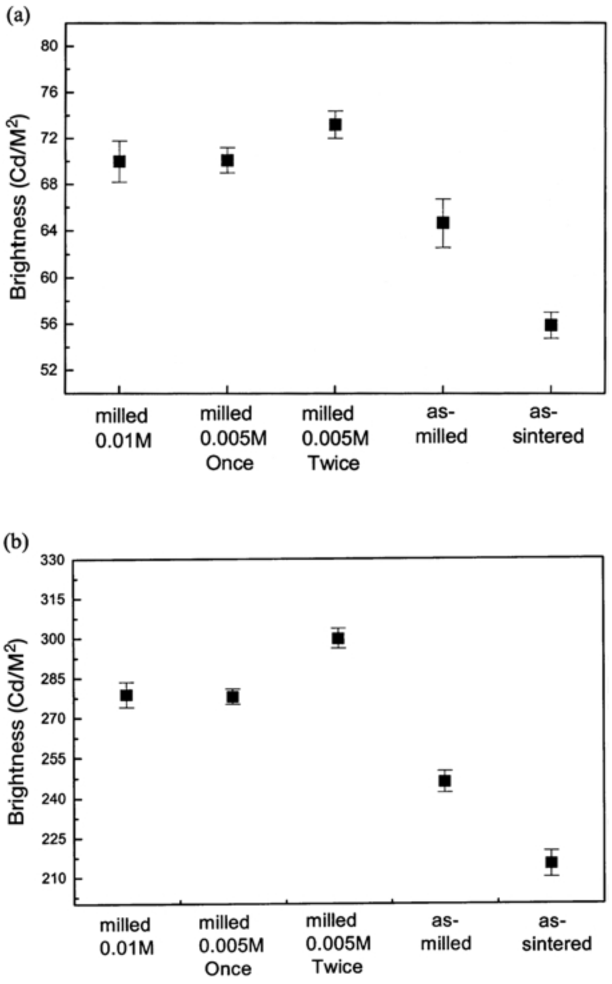

Figure 9 Brightness of ultrasonic-vibrated phosphors with one or two-step HNO_3 (0.01 M or 0.005 M) etching at: (a) 1 μA, 800 V and (b) 5 μA, 800 V.

The as-sintered phosphor has a range of particle size with an average of ∼ 17 μm. Agglomeration of powders is observed as shown in Fig. 1. Two methods, ball milling and ultrasonic vibration, were employed to break the agglomerates. Fig. 6 gives the particle-size distribution of the as-sintered, as-milled, and ultrasonic-vibrated phosphors. The average particle sizes are 6 and 15 μm for the as-milled and ultrasonic-vibrated phosphors, respectively. The brightness as a function of accelerating voltage is exhibited in Fig. 7. The as-milled phosphors have the lowest brightness among the three. The milling process may have damaged the surface of phosphors. While ultrasonic vibration appears to be an effective approach to break the agglomerates and enhances the brightness of phosphors.

Both the milled and ultrasonic-vibrated powders are then subjected to acid etching. Figs. 8 and 9 exhibit the brightness of phosphors after various treatments. Etching improves the brightness of the milled phosphor, however, the brightness is still smaller than that of the as-sintered one. Ultrasonic vibration followed by HNO_3 etching effectively improves the brightness of the phosphor. The brightness of the phosphor ultrasonically vibrated and then etched with 0.005 M HNO_3 twice increases ∼ 30% at 1 μA, 800 V and 40% at 5 μA, 800 V as compared to that of the as-sintered ones.

TABLE I Weight loss (%) of phosphors etched with HNO_3 or HCl of various concentrations

Acid Concentration (M)	HCl	HNO_3
0.05	53.5	72.7
0.03	26.4	39.2
0.01	11.9	12.4
0.005	4.9	5.7

4. Conclusions

In this study, three treatment methods have been carried out on ZnO : Zn phosphor; acid etching, milling, and ultrasonic vibration. Phosphor powders etched with HCl exhibit a rough surface, irregular shape, and poor brightness. However, brightness (25% at 5 μA, 800 V) increases for ZnO : Zn etched twice with 0.005 M HNO_3.

In breaking the phosphor agglomerates, ball milling reduces the particle size effectively, however, the decreased brightness suggests possible damage on the phosphor surface. Ultrasonic vibration breaks the agglomerates and enhances the brightness of the phosphors. The optimum treatment condition found is ultrasonic vibration followed by HNO_3 etching. A 40% increase in brightness is obtained for phosphor ultrasonically vibrated and then etched twice with 0.005 M HNO_3.

Acknowledgments

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