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Photoluminescence of $ZnGa_2O_4$ phosphor prepared by a microencapsulation method

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Abstract

An inorganic luminescent material has been prepared using the microencapsulation method. A chemical precipitation process was used to produce a uniform ZnO layer on the surface of Ga_2O_3 particles. The best encapsulating effect for Ga_2O_3 with particle size under 5 μm, is obtained with the use of urea concentration of 0.7 M in an 0.1 M $Zn(NO_3)_2{\cdot}6H_2O$ aqueous solution, heated at 75°C for 5–15 h. This composite powder requires a firing temperature of 1100°C and soaking time of 5 h, to synthesize phosphors with good repeatability. The synthetic $ZnGa_2O_4$ phosphor emits close to blue light at 455 nm under 254 nm excitation, and the best emission intensity is obtained when the molar ratio of ZnO/Ga_2O_3 approximately equals 1.0. The produced powder is anterior to the powder obtained by the traditional mechanical mixing which requires firing temperature above 1100°C with longer soaking time and emits a broad-band spectrum with a peak at 470 nm. © 2000 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

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1. Introduction

The preparation of inorganic luminescent materials normally uses mechanical mixing to make the starting powder. This process often causes homogeneity problems and vessel contamination by the powder, which in turn significantly influences the emission characteristics of the resulting phosphor.

Particle surface coating technique has been used to prepare coated powders by the chemical precipitation method. It is, precisely, a heterogeneous precipitation to encapsulate a uniform layer on the surface of stanting powders. This is also called the microencapsulation method [1–7]. It has an excellent position on the application of powder technology and the ceramic process. Fig. 1 shows schematic diagrams of a fired condition for (a) particle surface coating powder and (b) conventional mechanical mixing powder. The microencapsulation method can coat a uniform layer on the surface of each particle, so that each composite particle can react completely to get a homogeneously synthesized powder at firing treatment. Since the conventional mechanical mixing method is influenced by mixing degree, the synthesized powder can hardly get a homogeneous condition after firing.

Some of the recently published papers discuss the emission characteristics, crystal structure and preparation method of $ZnGa_2O_4$ phosphor [8–12]. In these preparation methods, mechanical mixing is used to make the raw powder. Therefore, the emission characteristics are influenced substantially by mixing degree and mixing condition. It is predicted that homogeneously composite powder can be made, and the disadvantage of mixing a solid powder in a mixing vessel can be avoided by using the microencapsulation method. The present work reports on the feasibility of using the microencapsulation method to substitute a conventional mechanical mixing method for the preparation of homogeneous and unpolluted composite powder of Ga_2O_3 particles with coated ZnO, which is then fired to become $ZnGa_2O_4$ phosphor.

2. Experimental procedure

The starting materials used were β-Ga_2O_3 (99.999%, $\geqslant$ 325 mesh, CERAC Ltd), $Zn(NO_3)_2{\cdot}6H_2O$ and $(NH_2)_2CO$ (both reagent grade, J.K. Baker Ltd), C_2H_5OH (99.5%, Seoul Chemical Co.).

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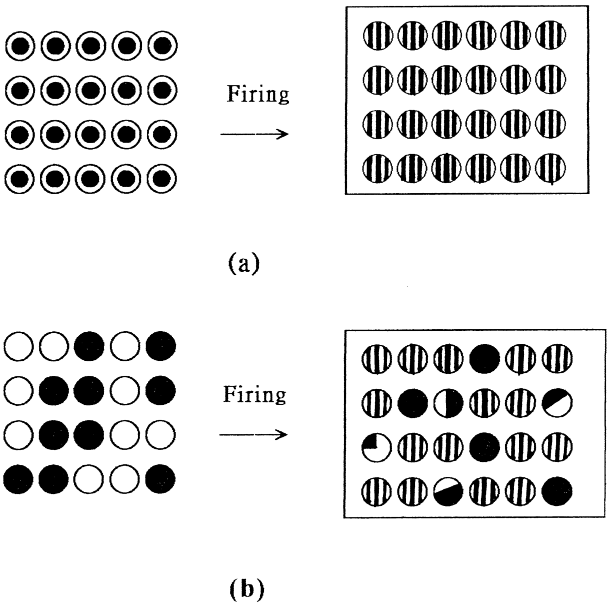


Fig. 1. Schematic diagrams of the fired powders formed from (a) uniformly coated inclusion particles and (b) conventional mixed powders.

An aqueous suspension solution containing 0.1 M $Zn(NO_3)_2$ $6H_2O$, 0.7 M urea, alcohol (half of aqueous solution) and a suitable amount of Ga_2O_3 powder was prepared and aged at 75°C with constant stirring for 5–15 h to produce a composite powder of Ga_2O_3 particles with coated ZnO. After aging, the suspension solution was cooled and the composite powder was filtered by vacuum filtration. The composite powder was washed with deionized water to remove excess solute and dried at 160°C for 20 h, then fired at 1100°C for 5 h in a covered alumina crucible to obtain homogeneous $ZnGa_2O_4$ phosphor powder.

The DTA analysis of the composite powder was measured by TA model 2000 thermal analyzer. A Hitachi S-800 scanning electronic microscope was used for scanning electron micrographs (SEM) analysis, in order to understand the encapsulating condition of the composite powder. The phase of the phosphors was characterized by X-ray diffractometry (XRD) analysis using Rigaku X-ray diffractometer with CuK_α radiation at 40 kV, 15 mA and 4°(2θ)/min scanning rate.

The photoluminescence emission and excitation spectra of the phosphors were obtained using a Shimadzu RF-5301PC spectrofluorophotometer. The excitation spectra could be obtained by scanning the wavelength from 220 to 800 nm monitored at 450 nm. The emission spectra were scanned from 400 to 800 nm excited at 245 nm.

3. Results and discussion

3.1. Preparation of coated ZnO on Ga_2O_3 particles

It is necessary to understand the chemical precipitation condition of ZnO before using the microencapsulation method. From the experiment, it shows that the particle size and amount of ZnO are influenced by urea concentration, heating temperature and aging time. Higher urea concentration and longer aging time can produce more ZnO as shown in Fig. 2. High heating temperature or long aging time will approach stoichiometry closely, and higher temperature will produce larger ZnO particles.

Based on the above result, the optimal condition has to be selected to prepare a composite powder of Ga_2O_3 with coated ZnO. This experiment selects an aqueous suspension solution containing 0.1 M $Zn(NO_3)_2$ $6H_2O$, 0.7 M urea and two particle sizes (under 5 μm and above 5 μm) of Ga_2O_3 powder and heating at 75°C with constant stirring for 5–15 h to produce powder mixture with ZnO/Ga_2O_3 molar ratios near to the equimolar quantities. Fig. 3 shows a SEM photograph of Ga_2O_3 particles with coated ZnO, which shows that the encapsulating effect is better for Ga_2O_3 particles under 5 μm and almost all particles are having the coated layer. For particle size above 5 μm, both encapsulating and mixing phenomena exist together. This result can be explained that: (1) the Ga_2O_3 particles under 5 μm have an appropriate surface area for heterogeneous nucleation of ZnO which occurs on the surface of Ga_2O_3 particles, and the deposition is continued to produce uniform layers of ZnO on Ga_2O_3; and (2) the particles of above 5 μm have not sufficient surface area to prevent the concentration of the reactant and to exceed the critical concentration homogeneous nucleation, so that a mixed system of free precipitates and coated particles is the result.

As for the Ga_2O_3 amount, about 3.4 g (42% of stoichiometry) of ZnO is formed at 0.1 M $Zn(NO_3)_2$

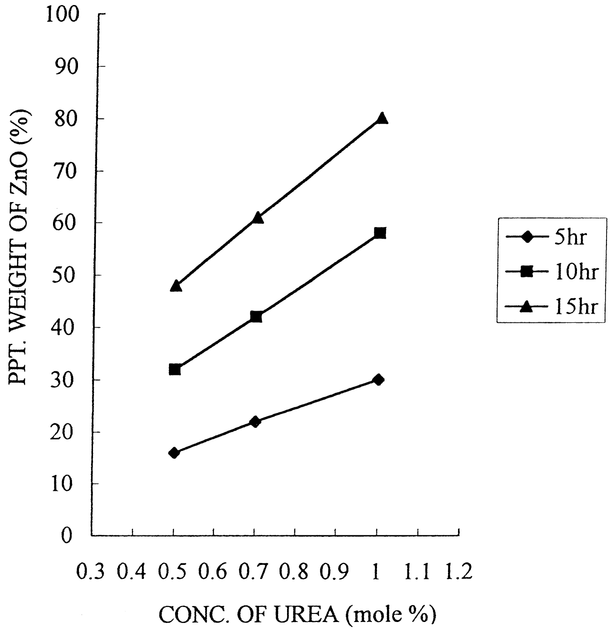
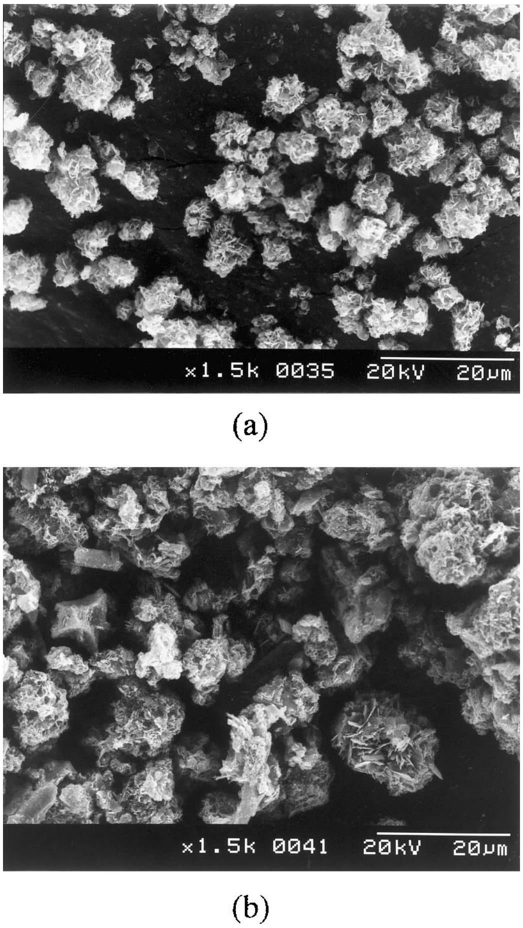


Fig. 2. Effect of urea concentration and aging time on the yield of the precipitated ZnO powder (heating temperature: 75°C).



(a)

(b)

Fig. 3. Scanning electron micrographs of the ZnO coated Ga_2O_3 particles. (a) Smooth coated inclusion particles; (b) a mixture of uncoated particles and coated particles.

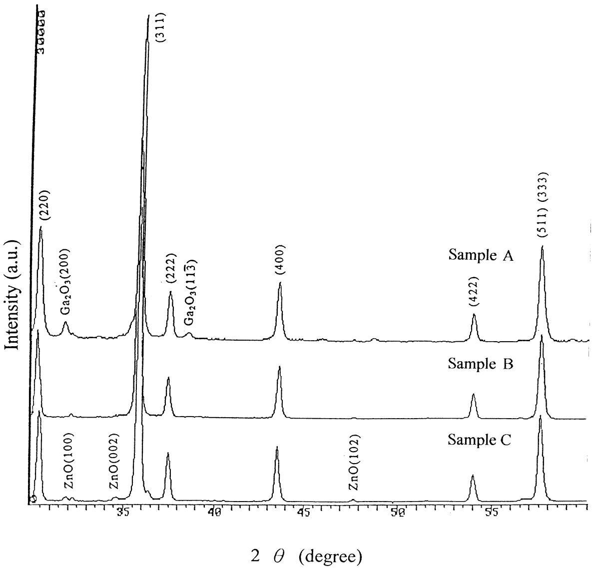


Fig. 4. X-ray diffractometry patterns of $ZnGa_2O_4$ with various molar ratios of ZnO/Ga_2O_3, prepared by the microencapsulation method.

$6H_2O$, 0.7 M urea, 75°C and 10 h of aging time. Based on this, a suitable amount of Ga_2O_3 is added to get the molar ratio of ZnO/Ga_2O_3 between 0.85/1.0 and 1.15/1.0. The amount of ZnO and Ga_2O_3 in the mixture is determined from the initial mass of the Ga_2O_3 powder used and the mass of the dried mixture.

3.2. Photoluminescence of synthesized $ZnGa_2O_4$ phosphors

The firing temperature of $ZnGa_2O_4$ phosphors synthesized by Ga_2O_3 with coated ZnO composite powder, can be obtained from the results of DTA analysis, the synthetic temperature when the molar ratio of $ZnO/Ga_2O_3 = 1.0/1.0$ is above 1030°C. Because of the relatively high vapor pressure, increased amounts of ZnO seemed to be lost during firing at high temperature, so that the optimal firing temperature was chosen as 1100°C. In previous studies, there have been cases in which the firing conditions were done at 1100°C for a long period (over 10 h) [8]. In order to understand the process and the result of firing Ga_2O_3 with coated ZnO composite powder to synthesize $ZnGa_2O_4$ phosphor, this study used 1100°C and different soaking time (3–10 h). The result shows that when firing at 1100°C and soaking time above 5 h, a pure $ZnGa_2O_4$ phosphor is obtained. Fig. 4 shows XRD patterns of $ZnGa_2O_4$ synthesized at 0.85/1.0, 1.0/1.0 and 1.15/1.0 molar ratios of ZnO/Ga_2O_3 obtained from 1100°C, with 5 h firing condition and summarized in Table 1. The crystal structure of sample B ($ZnO/Ga_2O_3 = 1.0/1.0$) has shown only the presence of $ZnGa_2O_4$ spinel phase. The three highest intensity peaks of $ZnGa_2O_4$ are the (220), (311) and (333) peaks. While sample A ($ZnO/Ga_2O_3 = 0.85/1.0$) and sample C ($ZnO/Ga_2O_3 = 1.15/1.0$), show some remaining Ga_2O_3 and ZnO, respectively. The above result is the same as the mechanical mixing powder sintered at 1300°C for 5 h [13].

The luminescent characteristic of the samples with various ZnO/Ga_2O_3 ratios is shown in Fig. 5. The absorption spectrum of sample B with pure $ZnGa_2O_4$ phase monitored at 450 nm exhibits a maximum absorption peak only at about 246 nm. Sample C not only introduce additional absorption peak at 320 nm due to the existence of ZnO minor phase, but also seriously decrease the intensity of both absorption peak and emission peak of $ZnGa_2O_4$ phosphors. Sample A with excess Ga_2O_3 also decrease the intensity.

Fig. 6 shows the emission spectra of $ZnGa_2O_4$ ($ZnO/Ga_2O_3 = 1.0/1.0$) phosphor prepared by the conventional mechanical mixing as well as the microencapsulation method. The emission spectra of both $ZnGa_2O_4$ phosphors under the exciting wavelength of 254 nm shows a broad-band emission, but the maximum emission peak and intensity are different. The conventional mechanical mixing $ZnGa_2O_4$ phosphor has a maximum emission

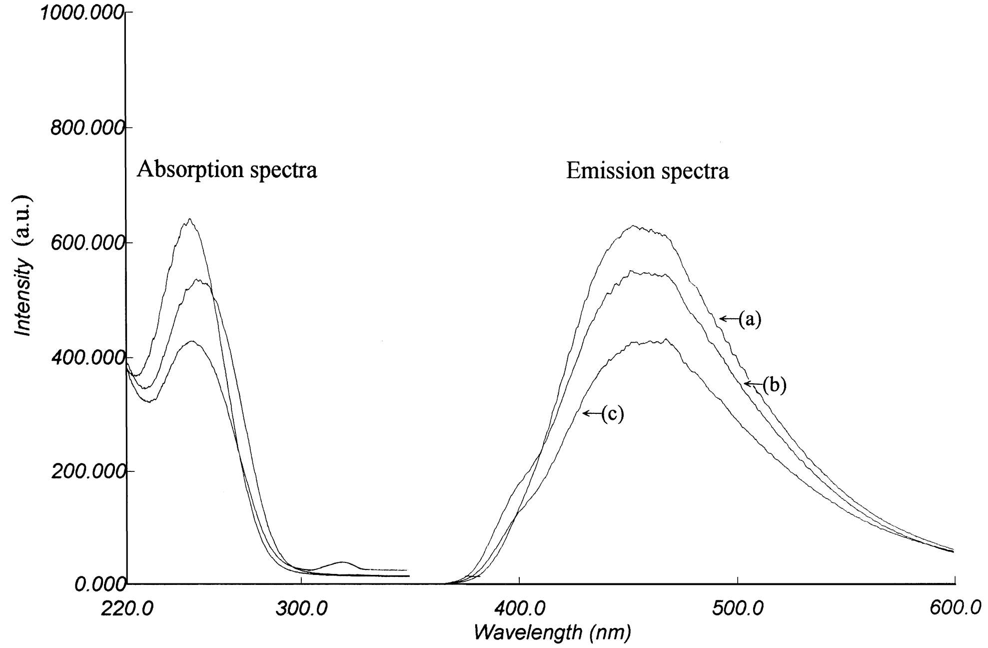


Fig. 5. Absorption and emission spectra of $ZnGa_2O_4$ phosphors prepared by the microencapsulation method. (a) Sample B; (b) sample A; (c) sample C.

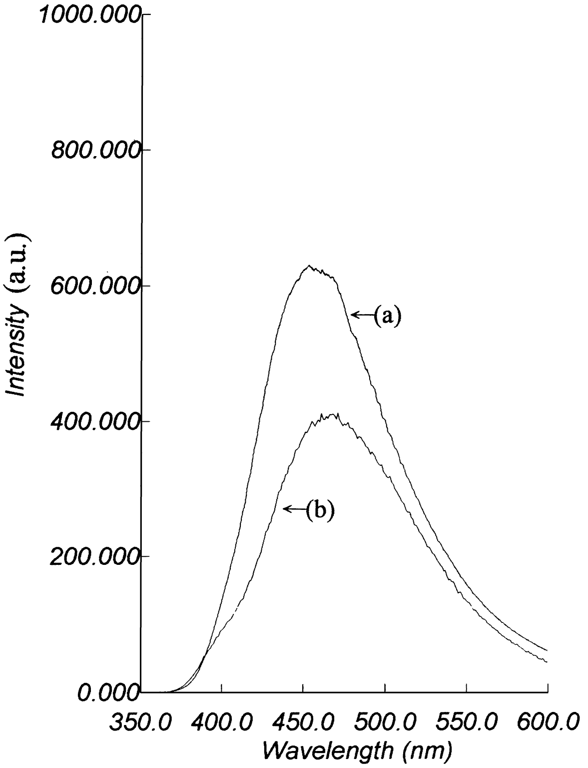


Fig. 6. Emission spectra of $ZnGa_2O_4$ ($ZnO/Ga_2O_3 = 1.0/1.0$) phosphors prepared by (a) the microencapsulation method (fired at 1100°C, 5 h) and (b) conventional method (fired at 1300°C, 5 h).

peak at 470 nm and of lower intensity. The microencapsulating $ZnGa_2O_4$ phosphor can get light more close to pure blue light at 455 nm and of higher intensity.

Table 1
Phase and emission intensity of fired zinc gallate samples

Samples	Composition (mol ratio)		Phases in the fired powders	Relative emission intensity
	ZnO	Ga_2O_3		
A	0.85	1.0	$ZnGa_2O_4 + \beta\text{-}Ga_2O_3$	88
B	1.0	1.0	$ZnGa_2O_4$	100
C	1.15	1.0	$ZnGa_2O_4 + ZnO$	67

4. Conclusions

In this paper the process to prepare $ZnGa_2O_4$ phosphor by the microencapsulation method has been reported. The result shows when urea concentration is 0.7 M in 0.1 M of $Zn(NO_3)_2\ 6H_2O$ aqueous solution, heating at 75°C, and the aging time is between 5 and 15 h, the encapsulation effect is better for Ga_2O_3 particles under 5 μm, and almost the entire surface of each particle has coated layer. The resulted composite powder can be synthesized to $ZnGa_2O_4$ phosphor at lower temperature (1100°C) and shorter time (5 h). The absorption spectrum of $ZnGa_2O_4$ phosphor has a peak at 246 nm, which was monitored at 450 nm. The peak emission spectrum is close to pure blue at 455 nm under 254 nm excitation, wherein the emission intensity is the best when molar ratio of ZnO/Ga_2O_3 approximately equals 1.0.

Acknowledgements

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