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Photoluminescence Characteristics of Nanocrystalline $ZnGa_2O_4$ Phosphors Obtained at Different Sintering Temperatures

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A nano-sized $ZnGa_2O_4$ phosphor was synthesized via a precipitation method (at a low temperature) and then sintered at various temperatures. X-ray diffraction (XRD) analysis confirmed that single-crystalline $ZnGa_2O_4$ particles were formed. A pure $ZnGa_2O_4$ phase was obtained at a sintering temperature of 1000°C. The average size of the spherical $ZnGa_2O_4$-phosphor particles increased with increasing sintering temperature. The most intense photoluminescence (PL) peak – corresponding to blue emission at about 420 nm – was observed for the sample prepared at a sintering temperature of 1000°C.

Keywords: field emission displays (FEDs); nanoparticles; phosphor; precipitation synthesis; $ZnGa_2O_4$

INTRODUCTION

Low-voltage field emission displays (FEDs) are among the most promising devices for fabricating flat-panel displays (FPDs) to replace the existing cathode-ray-tube (CRT) technology [1]. FEDs must operate at considerably lower excitation voltages and higher current densities than CRTs. Thus, compared to CRT phosphors, the

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phosphors for FEDs must have higher efficiency at low voltages, higher resolution, longer life-times, and equal or better chromaticity [2].

Sulfide phosphors are unsuitable for low-voltage applications, because the outgassing of sulfur-containing compounds from such phosphors may cause considerable damage to the cathodes and the phosphor surface. Oxide phosphors have the advantage that they are stable in high vacuum and do not emit corrosive gases under electron bombardment. Accordingly, low-voltage oxide phosphors have recently attracted much interest as possible alternatives to ZnS-based cathodoluminescent phosphors for low-voltage luminescence applications [3].

One well-known oxide phosphor is zinc gallate ($ZnGa_2O_4$), which has been studied for its good luminescent characteristics at low voltages [4,5]. $ZnGa_2O_4$ is a binary-compound oxide – consisting of ZnO and Ga_2O_3 – which crystallizes in a spinel structure. It has an energy band gap, E_g, of about 4.4 eV, and emits blue light as a result of transitions via a self-activation center. In addition, $ZnGa_2O_4$ shows emission from green to red when it is doped with Mn^{2+} and Cr^{3+} ions [6,7].

With the development of information displays, the phosphors have been required to provide effective excitation and absorption properties, suitable color purity, lower costs, longer lifetimes and better morphology, in which the size, the chemical composition, the form, and the surface properties all have important functions. Spherical particles can be easily densely packed, thus giving the screens and displays a higher definition; in addition, densely packed small particles can prevent the phosphors from aging [8].

Generally, $ZnGa_2O_4$-phosphor powders are produced on a large scale by means of conventional solid-state reactions, which means that multi-step processes, extremely high sintering temperatures, and relatively long times are required. Therefore, a simpler process was needed. Precipitation synthesis is one of the simplest powder-preparation methods available, in which the temperatures do not exceed 100°C and nanometer-sized crystals can be prepared. An attractive feature of this method is its ability to synthesize materials with high purity, good homogeneity, and high surface area in a single step.

In this study, $ZnGa_2O_4$ particles were synthesized under normal pressure using the precipitation method. The luminescence, formation process, and structure of the phosphor were evaluated for various sintering temperatures using X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM), and cathodoluminescence (CL).

EXPERIMENTAL

Synthesis

The nano-crystalline $ZnGa_2O_4$ phosphors were prepared by precipitation. $ZnSO_4 \cdot 7H_2O$ (99.99%, Aldrich) and $Ga_2(SO_4)_3 \cdot xH_2O$ (99.99%, Aldrich) were used as starting materials and aqueous NH_4OH (NH_3 content 28–30%, Sigma Aldrich) was used as the precipitant. The starting solutions were prepared by dissolving equimolar amounts of zinc sulfate and gallium sulfate in distilled water (final concentration 0.1 mol/dm^3) to give a metal-atom ratio of $Zn/Ga = 1/2$. A 0.89 mol/dm^3 aqueous ammonia solution was prepared and used in the experiments.

The starting metal solution was added to the aqueous ammonia solution at 90°C upon stirring (this was done at a rate of 1.5 ml/min and over 20 h). The metal ions were rapidly hydrolyzed by ammonia, and precipitation occurred spontaneously. The precipitation experiment was performed using a reflux system to preserve the concentrations over the experimental period. The precipitates were separated by filtration through a membrane filter, washed with distilled water, and then dried for 4 h in an oven at 60°C. The nanocrystalline $ZnGa_2O_4$ powders thus obtained were sieved to deagglomerate the particles and then sintered in furnace for 1 h, at temperatures between 400 and 1200°C.

Measurements

Phase identification of the particles at various sintering temperatures was performed by means of X-ray diffraction (XRD) using a Rigaku D/MAX-2200 diffractometer with CuKα radiation. The morphology and size of the prepared particles were investigated with field-emission scanning electron microscopy (FE-SEM, model S-4700, HITACHI). The photoluminescence (PL) measurements were carried out using a 150 W Xe lamp (spectrofluorometer, FP-6200, JASCO).

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of $ZnGa_2O_4$ samples sintered at different temperatures (between 400 and 1200°C). Spinel phases were obtained for all the as-prepared precipitates, and the diffraction peaks became sharper and stronger with increasing sintering temperatures as a result of an increase in crystallinity. However, at 1200°C, some additional small peaks corresponding to β-Ga_2O_3 were observed.

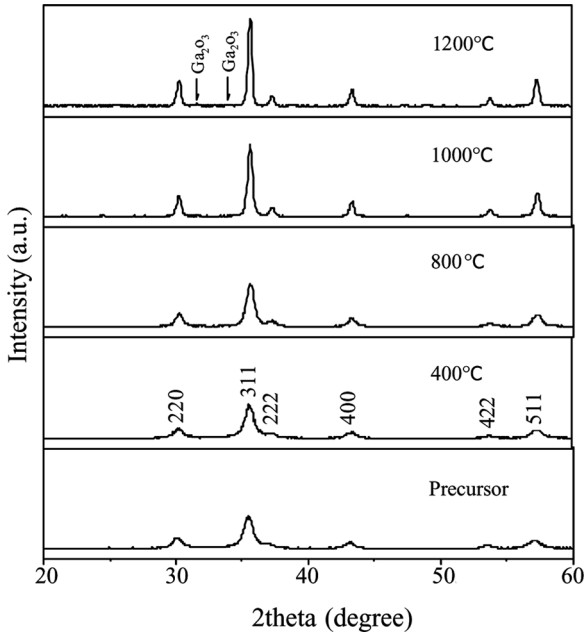

FIGURE 1 XRD patterns of $ZnGa_2O_4$ powders obtained at various sintering temperatures.

These signals can be explained by the fact that Zn^{2+} volatilizes at temperatures above 1200°C, which causes deficiencies of this ion in the spinel structure (i.e., Zn deficiency or Ga excess) [9].

The average grain sizes of the powders sintered at various temperatures were determined using the Scherrer's formula [7]. Scherrer's equation is applied to the (311) peaks in Figure 1. The dependence of the $ZnGa_2O_4$ crystallite calculation and real size on the sintering temperature is shown in the inset of Table 1.

TABLE 1 Particle Sizes of Nanocrystalline $ZnGa_2O_4$ Phosphors Obtained at Various Sintering Temperatures

Temperature (°C)	Calculation size (nm)	Real size (nm)
Precursor	12.8	15
400	13.1	25
800	14.2	40
1000	21.3	50
1200	25.3	200

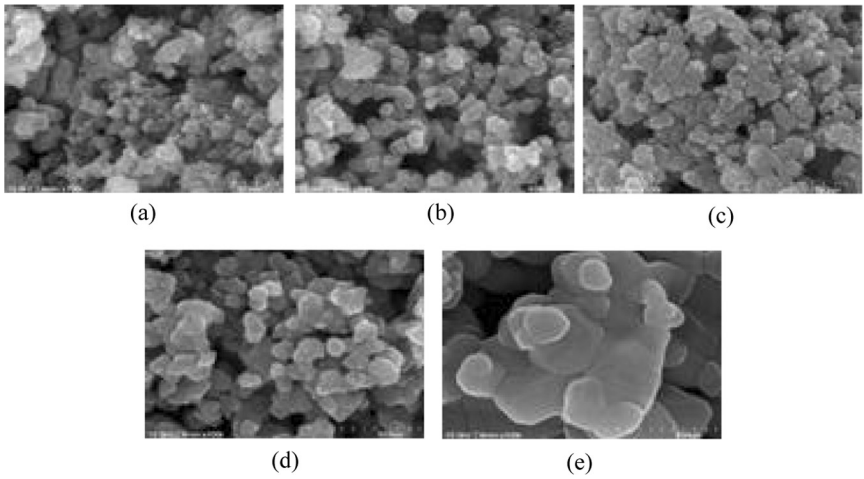

FIGURE 2 SEM images of $ZnGa_2O_4$ powders obtained at various sintering temperatures. (a) Precursor, (b) 400°C, (c) 800°C, (d) 1000°C, and (e) 1200°C.

Figure 2 shows SEM images of the different $ZnGa_2O_4$ samples. The size of the primary particles increased slightly with increasing temperature. At 1200°C, agglomerates formed and dramatic particle growth was observed. At this point, we estimated that the characteristics of the phosphor powders had been improved by increasing the sintering temperature; however, defects form in the phosphor when it is heated beyond a critical temperature [10]. The actual $ZnGa_2O_4$ particle size is about 50 nm at a sintering temperature of 1000°C, which is not consistent with the value calculated using Scherrer's formula. The size value obtained from FE-SEM measurements is larger than that determined from the XRD patterns. The latter value is a calculated result, which reveals the size of a single particle, whereas the former one is an observed result which shows the actual morphology, including aggregation [8].

Figures 3 and 4 show, respectively, a PL excitation spectrum (at 292 nm) and PL emission (PLE) spectra of $ZnGa_2O_4$ nano-particles sintered at various temperatures. The emission spectrum of $ZnGa_2O_4$ shows a narrow, self-activated blue emission band around 420 nm, which can be attributed to the presence of Ga^{3+} at the octahedrally coordinated site [5]. The intensity of this band was observed to increase with increasing sintering temperature, reaching its maximum at 1000°C. However, because of growth defects found at high temperatures and as a result of the increase in the nonradiative recombination

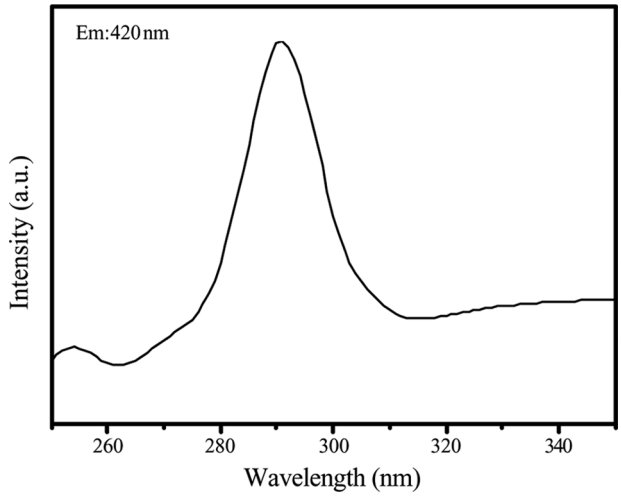

FIGURE 3 PL excitation spectrum of $ZnGa_2O_4$ powders.

of the grain boundaries, the emission band at 420 nm became weaker at a sintering temperature of 1200°C [11]. These results are consistent with those obtained from XRD and SEM measurements.

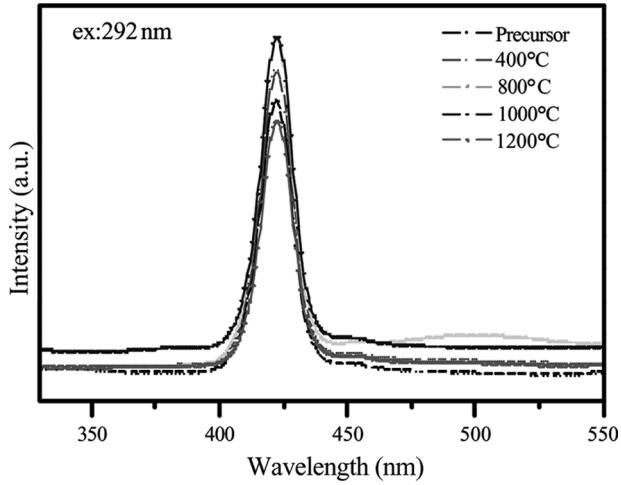

FIGURE 4 PL emission spectra of $ZnGa_2O_4$ powders obtained at various sintering temperatures.

CONCLUSIONS

A nanosized $ZnGa_2O_4$ phosphor was synthesized through a precipitation method (at a low temperature) and then sintered at various temperatures. Ideal spinel structures and spherical nanoparticles with an average size of about 50 nm were obtained at a sintering temperature of 1000°C. The PL intensity was observed to increase with increasing sintering temperature (up to 1000°C), but a quenching effect appeared at 1200°C. This phenomenon was attributed to defects at high temperatures and to an increase in the nonradiative recombination of the grain boundaries.

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