Self-Regulation Synthesis of Nanocrystalline $ZnGa_2O_4$ by Hydrothermal Reaction

Yadong Li,* Xiangfeng Duan, Hongwei Liao, and Yitai Qian

Department of Chemistry and Structure Research Laboratory University of Science and Technology of China Hefei Anhui 230026, P.R. China

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Introduction

$ZnGa_2O_4$ as a good low-voltage phosphor material used in a new kind of vacuum flat cathode ray tube of the field emission display has attracted a wide range of interest.[1−3] Various powders and films of $ZnGa_2O_4$ with low-voltage cathode luminescence have been explored.[3−6] However, the reported preparation methods of $ZnGa_2O_4$ powder were traditional solid-state reaction methods. As we know, different material preparation methods have important effects on material microstructure and physical properties. Recently, there is a strong trend toward the application of solution chemical synthesis techniques for materials preparation.[7,8] Hydrothermal method is one of the most promising solution chemical methods. The particles size and their distribution, phase homogeneity, and morphology could be well controlled.[7−9] We have successfully synthesized the InAs nanocrystalline by this chemical method.[10]

This paper describes the low temperature hydrothermal synthesis of the nanocrystalline $ZnGa_2O_4$ with Zn powder as chemical self-regulation reagent in the $GaCl_3$ chlorohydric acid aqueous solution. The hydrothermal synthesis of $ZnGa_2O_4$ is associated with the chemical reaction

$$4Zn + 2GaCl_3 + 4H_2O \rightarrow ZnGa_2O_4\downarrow + 4H_2\uparrow + 3ZnCl_2$$

In this process, not only can the Zn^{2+} ion concentration and the pH value of the solution be self-regulated but also the nucleation of $ZnGa_2O_4$ crystalline and its growth can be well self-controlled.

Experimental Section

An appropriate amount of Ga (99.99%) was dissolved in chloride acid solution to form 0.1 M $GaCl_3$ aqueous solution (pH < 1), 150 mL of 0.1 M and 2.2 g (about 0.033 mol) analytical grade zinc powder were put into a Teflon liner hydrothermal actoclave of 300 mL capacity. The autoclave was kept constantly at 150 °C (the pressure in autoclave is about 4.76 atm) for 10 h and then cooled to room temperature naturally. The product was filtered and washed with dilute HCl aqueous solution and then washed free of chloride ion with distilled water, the product was oven-dried at 100 °C for 4 h. A gray white product was obtained.

The obtained samples were characterized by the X-ray powder different (XRD) method. The XRD was carried out with a Japan Rigaku D/max-rA rotation anode X-ray diffractometer, using Ni-filtered Cu Kα radiation. A scan rate of 0.05°/s was applied to record the patterns in the 2θ range 10−70°. The morphology and particle size of $ZnGa_2O_4$ were determined by transmission electron microscopy (TEM). The images were taken with Hitachi H − 800 transmission electron microscope. The pH value was determined by means of a precise pH meter.

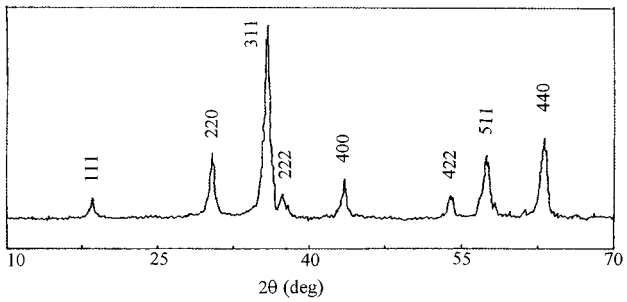

Figure 1. XRD pattern of the sample $ZnGa_2O_4$.

Results and Discussion

$ZnGa_2O_4$ with the formula AB_2O_4 has a cubic structure that can be viewed as a combination of rock salt and zinc blende structures, a normal spinel structure. The oxygen ions are in face-centered cubic closed packing. All of the Zn^{2+} ions are in A site (tetrahedral site), Ga^{3+} ions in B sites (octahedral site), and the lattice constant $a = 0.8335$ nm.

Figure 1 shows the XRD patterns of a typical sample prepared by the hydrothermal process. All the peaks could be indexed as the spinel $ZnGa_2O_4$ phase, and after refinement the cell constant $a = 0.8334$ nm was closed to that reported in the literature[3] (JCPDS, 38-1240). No impurity XRD peaks such as Zn,Ga_2O_3, ZnO were detected. The XRD peaks of spinel $ZnGa_2O_4$ were broad in accordance with their small grain size and low degree of crystallinity. The crystallite size of spinel $ZnGa_2O_4$ was estimated by the Scherrer equation.[7] The estimated grain size was 10 nm, in excellent agreement with that observed from TEM images.

Figure 2 was the TEM microphoto of as-prepared spinel $ZnGa_2O_4$ particles. The particles in the microphoto are nonagglomerative spherical. One could see that the morphology was homogeneous; the average size was about 10 nm.

The products were weighed and the yield was calculated (based on the molar weight of $GaCl_3$). The results showed that the yield of $ZnGa_2O_4$ was above 95% (if based on Zn, the theoretical yield of $ZnGa_2O_4$ is about 86%). During the hydrothermal process of the self-regulation synthesis of $ZnGa_2O_4$, several factors such

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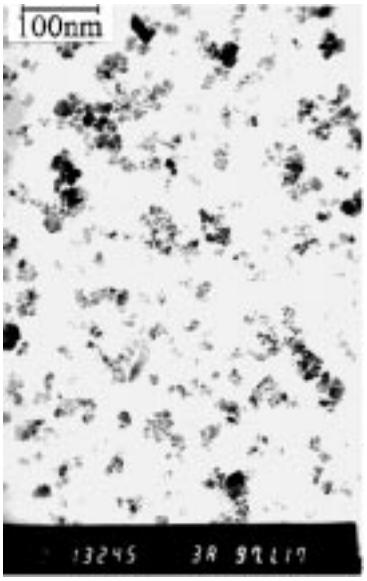

Figure 2. TEM image of the sample $ZnGa_2O_4$.

as temperature, pH values, the amount of Zn powder, and the self-regulation mechanism of the synthesis reaction should be considered. When the temperature was below 130 °C, the reaction was very slow and not complete, and the yield was very low. If the temperature was above 180 °C, the size of the products was large. The optimum temperature for preparing nanocrystalline $ZnGa_2O_4$ was in the range 140−170 °C. So we chose 150 °C as the optimum hydrothermal synthesis temperature of nanocrystalline $ZnGa_2O_4$.

The pH value and the amount of zinc powder were the critical factors in the formation of spinel $ZnGa_2O_4$ and its growth. When the pH value of $GaCl_3$ aqueous solution was above 3, Ga^{3+} precipitated as $Ga(OH)_3$, at 150 °C, $Ga(OH)_3$ could decompose to form Ga_2O_3. The yield of the $ZnGa_2O_4$ and the purity of the product were directly affected. The initial feedstock pH ($GaCl_3$ solution) below 1.0 was selected. In the hydrothermal synthesis process, adding the appropriate amount of zinc powder could self-regulate the pH value of the hydrothermal reaction system to a optimum pH range (pH 3.5−7.0). It is according to the following reaction:

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2\uparrow$$

$$ZnCl_2 + 2GaCl_3 + 4H_2O \rightarrow ZnGa_2O_4 + 8HCl$$

The Zn^{2+} and the pH value of the reaction system could be self-regulated by the above reactions. At the same time, the nucleation and growth of crystalline $ZnGa_2O_4$ in this process were well controlled.

From the above self-regulation mechanism of the formation of $ZnGa_2O_4$ crystalline in the hydrothermal process. We name the following reaction:

$$4Zn + 2GaCl_3 + 4H_2O \rightarrow ZnGa_2O_4\downarrow + 3ZnCl_2 + 4H_2\uparrow$$

as self-regulation synthesis of $ZnGa_2O_4$ crystalline. To maintain the above reaction proceeding completely, the amount of zinc powder was excessive compared with the amount of $2GaCl_3$. The optimum amount of zinc powder was 10−20% excess of the calculated amount. For example, for a solution of 0.015 mol of $2GaCl_3$ and 0.033 mol (2.2 g) of zinc powder was needed. When the amount of zinc powder was less than the optimum amount, the synthesis reaction was not complete and the yield was low. A more excessive amount of zinc powder was not needed and it could make the purification of the products more difficult.

Conclusion

Nanocrystalline $ZnGa_2O_4$ were synthesized successfully by a self-regulation hydrothermal reaction at 150 °C. The results of the XRD and TEM indicated that the product was nonagglomerative spherical: the average particle size was 10 nm. The simplicity of the process and high yield make it possible for industrial application.

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