

Hydrothermal synthesis and characterization of ZnGa₂O₄ spinel fine particles

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The influences of solution pH, cation concentration, treatment temperature, time, and ZnO/Ga₂O₃ molar ratio of the starting solution on the crystallite size, morphology, lattice parameters and chemical composition of hydrothermally synthesized ZnGa₂O₄ spinel particles were investigated. Nanocrystalline ZnGa₂O₄ spinel particles were prepared from gallium sulfate and zinc sulfate in the presence of aqueous ammonia under hydrothermal conditions in the pH range of 2.5 to 10. Their crystallite size increased and their chemical composition approached ZnO/Ga₂O₃ = 1 with increasing treatment temperature, time, and starting ZnO/Ga₂O₃ molar ratio. ZnGa₂O₄ spinel particles with a stoichiometric composition were synthesized by controlling the starting ZnO/Ga₂O₃ molar ratio under hydrothermal conditions at 240 °C for 50 h. The formation mechanism of the ZnGa₂O₄ spinel particles was discussed, and the diffusion of Zn²⁺ ions seemed to be the key for the synthesis and growth of the spinel, especially for obtaining a stoichiometric composition.

Introduction

ZnGa₂O₄ is a double oxide with the cubic spinel structure¹ and one of the new transparent and conductive materials.² It has various applications, such as transparent electrodes in liquid crystal displays (LCD) and solar cells, because of its optical transparency and metallic conductivity. Many fundamental studies have been reported on the synthesis and the electrical and optical properties of the ZnGa₂O₄ spinel. It has also attracted interest as a good low-voltage phosphor material³ used in a new kind of vacuum flat cathode ray tube. The optical bandgap of ZnGa₂O₄ is about 4.4 eV. It shows emission from green to red when it is doped with Cr and Mn, though it shows blue emission without any dopant.

The synthesis of ZnGa₂O₄ spinel has been done mostly by a solid-state reaction between two metal compounds, *e.g.* zinc oxide and gallium oxide,²⁻⁴ and also by pulverizing single crystals synthesized by the flux method⁵⁻⁷ using Li₃PO₄ at high temperatures. Thin films of ZnGa₂O₄ spinel have been prepared by the sol-gel⁸ and sputtering processes.⁹ The method of precipitation from solution under hydrothermal conditions is of current interest and attractive for the direct synthesis of crystalline ceramic particles during the reaction at relatively low temperatures. Hydrothermal reactions in general are carried out in an autoclave at temperatures between the boiling and critical points of water (100 to 374 °C) and at elevated pressures (up to *ca.* 15 MPa). The powder synthesized by this method has excellent homogeneity and particle uniformity. This hydrothermal route has been used for the synthesis of fine oxide powders, and their particle size and morphology could be well controlled.¹⁰⁻¹³ We have reported the preliminary results of the hydrothermal synthesis of ZnGa₂O₄ spinel particles.¹⁴ Through this chemical route, there is the possibility for the direct synthesis of stoichiometric ZnGa₂O₄ spinel fine particles.

In the present study, to efficiently synthesize ZnGa₂O₄ spinel fine particles at a relatively low temperature, the effects of temperature, time, cation concentration, ZnO/Ga₂O₃ molar ratio, and solution pH on the morphology, crystal growth, composition, and lattice parameters of the ZnGa₂O₄ spinel particles were investigated.

Experimental

Sample preparation

Zinc sulfate (ZnSO₄·7H₂O, High Purity Chemicals Laboratory, Japan, purity greater than 99.9%) and gallium sulfate (Ga₂(SO₄)₃·12H₂O, High Purity Chemicals Laboratory, Japan, purity greater than 99.99%) were used as the raw materials. Zinc sulfate and gallium sulfate in a certain ZnO/Ga₂O₃ molar ratio were dissolved in distilled water in a Teflon vessel. The desired amount of aqueous ammonia (28 wt% NH₃) was poured into this solution to control the solution pH. This mixed solution with the desired concentration was then placed in a stainless steel vessel. After the vessel was sealed, it was placed in a thermostatted oven, and heated at 150 to 240 °C for 5 to 50 h with constant rotation. The precipitated solid product was separated by centrifuging, washed, and then dried in an oven at 60 °C in air.

Sample characterization

Phase identification was performed by X-ray powder diffraction (XRD) using Cu-K α radiation. The crystallite size was calculated from the line broadening of the 400 diffraction line according to the Scherrer equation. The lattice parameters were measured from the 400 diffraction line using silicon as the internal standard. The morphology and size of the precipitates were examined using transmission electron microscopy (TEM; model JEM-200CX, JEOL, Tokyo, Japan). The overall ZnO/Ga₂O₃ molar ratio of the precipitates was examined by X-ray fluorescence analysis.

Results

Influence of pH and concentration

The effect of the solution pH on the phase of the solid precipitates formed at 200 °C for 20 h from the mixed solutions of 0.2 mol dm⁻³ Ga₂(SO₄)₃ and 0.3 mol dm⁻³ ZnSO₄, *i.e.* ZnO/Ga₂O₃ = 1.5, is shown as the XRD patterns in Fig. 1. It was confirmed that a ZnGa₂O₄ spinel single phase, with no extra peaks such as ZnO and GaO(OH), was synthesized over the pH range 2.5 to 10. The ZnGa₂O₄ spinel was the main

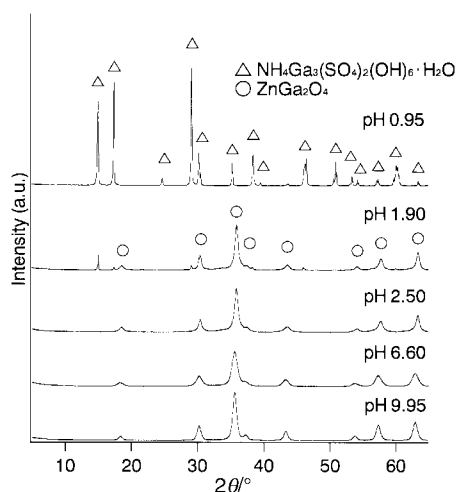


Fig. 1 XRD patterns of the solid products formed by hydrothermal treatment at 200 °C for 20 h at various pH values from mixed solutions of 0.2 mol dm⁻³ Ga₂(SO₄)₃ and 0.3 mol dm⁻³ ZnSO₄.

precipitate phase at pH 1.9, together with a small amount of $\text{NH}_4\text{Ga}_3(\text{SO}_4)_2(\text{OH})_6 \cdot \text{H}_2\text{O}$, though a single phase of $\text{NH}_4\text{Ga}_3(\text{SO}_4)_2(\text{OH})_6 \cdot \text{H}_2\text{O}$ was precipitated at pH 0.95. The XRD peaks of the spinel were broad in accordance with their small crystallite size and low degree of crystallinity. It is seen from the line broadening in the XRD pattern that the spinel particles synthesized from the basic solution (pH 9.95) and acid solution (pH 2.5) had a higher degree of crystallinity than those from the neutral solution (pH 6.6). The influence of solution pH on the growth of the spinel particles is shown in the TEM photographs in Fig. 2, in which the particles were synthesized under the same conditions except for the concentration of aqueous ammonia. It is clear that the spinel particles formed in the basic solution at pH 9.95 (Fig. 2(b)) grew larger than those in the neutral solution at pH 6.6 (Fig. 2(a)).

For a constant ZnO/Ga₂O₃ molar ratio (*i.e.* ZnO/Ga₂O₃ = 1.5) in the starting solution, the effect of the cation concentration on the crystallite size of the synthesized spinel particles (calculated from the XRD line-broadening of the 400 diffraction line) is revealed in Fig. 3 as a function of the ZnSO₄ concentration. This shows that the crystallite size depended on the concentration, and it gradually decreased to about one third for a concentration change of 0.05 to 0.5 mol dm⁻³. The particle size determined by X-ray line broadening was in fairly good accordance with that determined from TEM observation, showing that the particles observed in the TEM photographs were single crystals.

Influence of reaction temperature and time

In Fig. 4, the crystallite size of the synthesized spinel particles is plotted *versus* the hydrothermal treatment temperature, showing that the particles grew larger with increasing temperature. The effect of treatment time on the morphology and size of the synthesized particles is shown in the TEM photographs of Fig. 5. Although the XRD data of the specimens shown in Fig. 5 were all characteristic of the ZnGa₂O₄ spinel structure without any other phases, some elongated or rod-like particles were observed in the specimen formed at 200 °C for 5 h (Fig. 5(a)). As shown in Fig. 5(b), the particles became thick and roundish, and increased in size upon treatment for 50 h at the same temperature, in which elongated particles could not be detected.

In Fig. 6, the lattice parameters of the ZnGa₂O₄ spinel particles synthesized at different temperatures are plotted as a function of hydrothermal treatment time. With increasing treatment time and temperature, the lattice parameter increased and approached the value $a = 0.83349$ nm as reported

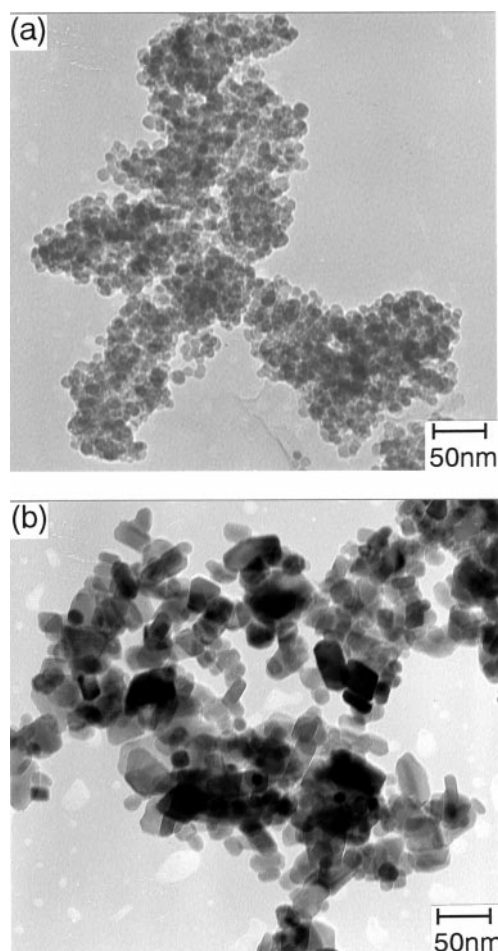


Fig. 2 TEM photographs of ZnGa₂O₄ spinel particles prepared at 240 °C for 20 h from mixed solutions of 0.2 mol dm⁻³ Ga₂(SO₄)₃ and 0.3 mol dm⁻³ ZnSO₄ (a) in the presence of 2.5 mol dm⁻³ aqueous ammonia (pH 6.6) and (b) 4.1 mol dm⁻³ aqueous ammonia (pH 9.95).

in the literature.¹⁵ For the highest temperature of 240 °C and the longest treatment time of 50 h, a value of $a = 0.8328$ nm was obtained. However, under this preparation condition, *i.e.*, ZnO/Ga₂O₃ = 1.5, the lattice parameters obtained from the specimens were not in accordance with the reported value.¹⁵

Influence of ZnO/Ga₂O₃ molar ratio

In Fig. 7, the crystallite sizes of the ZnGa₂O₄ spinel particles synthesized at 200 °C and 240 °C are plotted *versus* the ZnO/

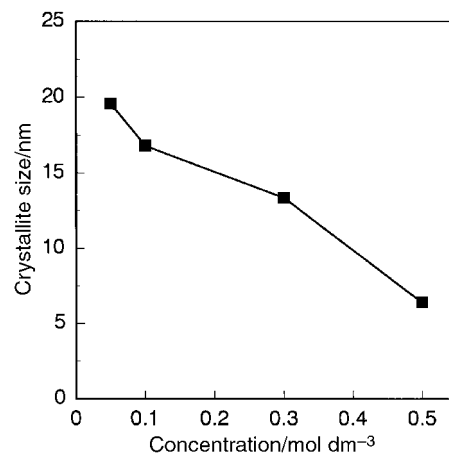


Fig. 3 Crystallite size of the spinel particles prepared at 200 °C for 10 h at ZnO/Ga₂O₃ = 1.5 at around pH 10 as a function of the ZnSO₄ concentration.

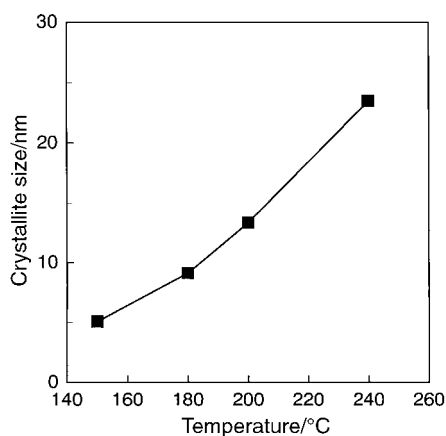


Fig. 4 Effect of hydrothermal treatment temperature on the crystallite size of the spinel particles synthesized for 10 h from mixed solutions of $0.2 \text{ mol dm}^{-3} \text{ Ga}_2(\text{SO}_4)_3$ and $0.3 \text{ mol dm}^{-3} \text{ ZnSO}_4$ in the presence of 4.1 mol dm^{-3} aqueous ammonia.

Ga_2O_3 molar ratio in the starting solution, showing that the crystallite size increased with an increase in the $\text{ZnO}/\text{Ga}_2\text{O}_3$ molar ratio. The spinel particles grew large and became roundish with increasing $\text{ZnO}/\text{Ga}_2\text{O}_3$ molar ratio.

The relation between the $\text{ZnO}/\text{Ga}_2\text{O}_3$ molar ratio of the starting solution and the $\text{ZnO}/\text{Ga}_2\text{O}_3$ molar ratio in the solid product, quantitatively analyzed using X-ray fluorescence, is shown in Fig. 8. With increasing $\text{ZnO}/\text{Ga}_2\text{O}_3$ starting ratio and treatment temperature, the $\text{ZnO}/\text{Ga}_2\text{O}_3$ ratio of the synthesized particles increased and approached 1.0, *i.e.*, the stoichiometric composition of the ZnGa_2O_4 spinel. The lattice parameter of the ZnGa_2O_4 spinel particles synthesized at 240°C increased with increasing $\text{ZnO}/\text{Ga}_2\text{O}_3$ ratio and almost reached the value ($a = 0.83349 \text{ nm}$)¹⁵ of the stoichiometric composition of the ZnGa_2O_4 spinel.

Discussion

It is important to note that the nanocrystalline ZnGa_2O_4 spinel particles are formed in the relatively wide pH range of 2.5 to 10. The crystallite size dependence on the cation concentration shown in Fig. 3 may be explained by the following reason. The degree of supersaturation was low for the lower reactant concentration, so the nucleation number was less and the particles tended to grow in size. The growth in crystallite size with increasing treatment temperature shown in Fig. 4 can be mainly explained by a solution and precipitation mechanism.

In a previous report,¹⁶ the solid products gradually changed from $\text{GaO}(\text{OH})$ to ZnGa_2O_4 with increasing treatment temperature from 100 to 180°C , though the main solid product was $\text{GaO}(\text{OH})$ in the specimens treated at 100°C , together with a very small amount of fine ZnGa_2O_4 detected as a broad peak at around $2\theta = 36^\circ$. The precipitates obtained at temperatures above 180°C exhibited all the diffraction lines for ZnGa_2O_4 with a cubic spinel structure, with no extra peaks, though ZnGa_2O_4 and a small amount of $\text{GaO}(\text{OH})$ are recognized to coexist in the precipitates treated at 150°C .¹⁶ Ga^{3+} ions form the hydroxide at low pH (*i.e.*, pH 3 to 12–13); on the other hand, Zn^{2+} ions form the hydroxide at pH 6.5 to 14 according to earlier work.¹⁷ At the stage before the reaction between Ga and the Zn source, a certain amount of gallium hydroxide (*i.e.*, amorphous gallium hydroxide gel, crystalline $\text{GaO}(\text{OH})$) and zinc hydroxide exist in the presence of aqueous ammonia; however, zinc hydroxide is thought to be more easily dissolved and to more readily form complex ions than gallium hydroxide upon the dropwise addition of concentrated aqueous ammonia.

What is significant about the facts obtained in this work and a previous report¹⁶ is that (1) there existed no solid crystalline phase containing the Zn element in the solid products except

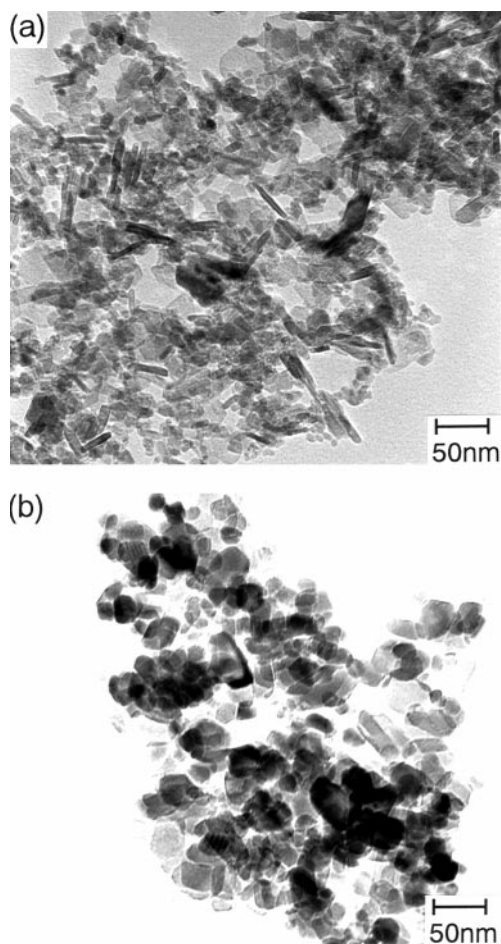


Fig. 5 TEM photographs of ZnGa_2O_4 spinel particles prepared at 200°C for (a) 5 h and (b) 50 h from mixed solutions of $0.2 \text{ mol dm}^{-3} \text{ Ga}_2(\text{SO}_4)_3$ and $0.3 \text{ mol dm}^{-3} \text{ ZnSO}_4$ in the presence of 4.1 mol dm^{-3} aqueous ammonia.

for the ZnGa_2O_4 spinel through all the treatment, (2) the crystalline solid precipitates formed at the low temperature of 100°C consisted mainly of $\text{GaO}(\text{OH})$ together with a small amount of the ultra-fine ZnGa_2O_4 spinel, (3) the ZnGa_2O_4 spinel phase increased with decreasing $\text{GaO}(\text{OH})$ phase, (4) elongated spinel particles with a nonstoichiometric composition poor in Zn concentration, in which the morphology is relatively similar to the needle-like $\text{GaO}(\text{OH})$ particles, are present in the specimens treated under relatively soft hydrothermal conditions as shown in Fig. 5(a), and (5) the shape of some ZnGa_2O_4 spinels changed from elongated particles to

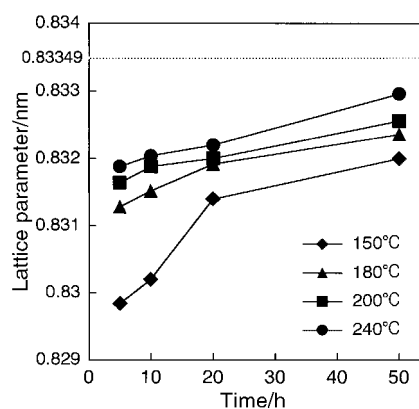


Fig. 6 Effect of hydrothermal treatment time on the lattice parameter of the spinel particles synthesized at various temperatures from mixed solutions of $0.2 \text{ mol dm}^{-3} \text{ Ga}_2(\text{SO}_4)_3$ and $0.3 \text{ mol dm}^{-3} \text{ ZnSO}_4$ in the presence of 4.1 mol dm^{-3} aqueous ammonia.

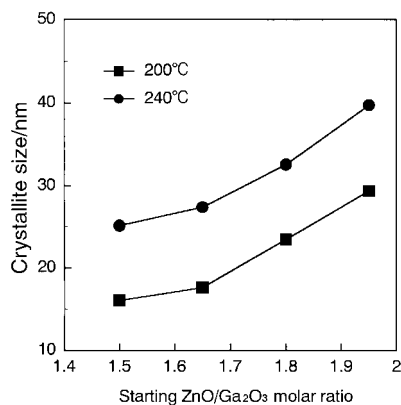


Fig. 7 Crystallite size of ZnGa₂O₄ spinel particles synthesized at 200 °C and 240 °C for 20 h using a constant solution of 0.2 mol dm⁻³ Ga₂(SO₄)₃ in the presence of 4.1 mol dm⁻³ aqueous ammonia as a function of ZnO/Ga₂O₃ molar ratio in the starting solution.

cubic or octahedral in appearance. On the basis of these facts, one possible scenario for the formation of the ZnGa₂O₄ spinel particles under hydrothermal conditions is proposed. ZnGa₂O₄ spinel nuclei are formed during the first stage of the reaction. The dissolved Zn(OH)₂ or Zn²⁺ complex ions are transported to the surface of the amorphous gallium hydroxide gel and needle-like GaO(OH) particles in the solution. The zinc gallate cluster, which is the embryo, is then formed by the reaction of these gallium hydroxides with Zn²⁺ ions on their surfaces. The size of the cluster becomes larger than that of the critical nucleus, becomes a stable nucleus and begins to grow. By growth of the nucleus, granular and rod-like spinel particles with a cubic phase having a nonstoichiometric composition are formed based on the structure of the amorphous gallium hydroxide gel and needle-like GaO(OH) particles, respectively. According to the solution and precipitation mechanism, these spinel particles, including elongated particles, grow large and thick, their shapes become roundish, and their composition approaches stoichiometry by the continuous diffusion of Zn²⁺ ions. The existence of the elongated or rod-like spinel particles shown in Fig. 5(a) might be evidence that they grew from the base structure of the needle-like GaO(OH) particles by a hydrothermal reaction.

According to the above scenario, the diffusion of Zn²⁺ ions seems to be the key for the synthesis and growth of the spinel, especially for obtaining a stoichiometric composition. With increasing reaction temperature accompanying a pressure increase, and increasing reaction time, ZnGa₂O₄ spinel particles increased in size while approaching the stoichiometric composition. Increasing the ZnO/Ga₂O₃ ratio in the starting solution, *i.e.* increasing the Zn²⁺ concentration, causes a high

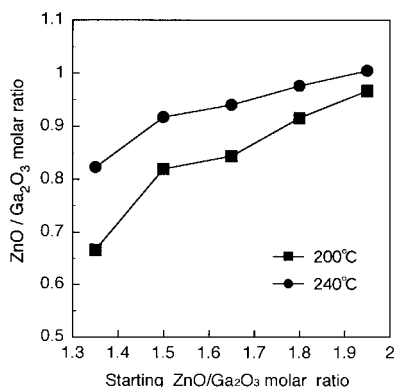


Fig. 8 ZnO/Ga₂O₃ molar ratio of the particles synthesized at 200 °C and 240 °C for 20 h using the constant solution of 0.2 mol dm⁻³ Ga₂(SO₄)₃ in the presence of 4.1 mol dm⁻³ aqueous ammonia as a function of the ZnO/Ga₂O₃ molar ratio in the starting solution.

diffusion rate for the Zn²⁺ passing per unit time through a unit area, as the average diffusion distance for the diffusing solute is short. Finally, ZnGa₂O₄ spinel particles with the composition ZnO/Ga₂O₃=1 and lattice parameter $a=0.83349$ nm could be synthesized from the relatively concentrated solutions, *e.g.*, 0.2 mol dm⁻³ Ga₂(SO₄)₃, and at ZnO/Ga₂O₃=1.95, under hydrothermal conditions at 240 °C for 50 h.

Summary

ZnGa₂O₄ spinel fine particles were prepared from gallium sulfate and zinc sulfate in the presence of aqueous ammonia under hydrothermal conditions. The influences of solution pH, cation concentration, and starting ZnO/Ga₂O₃ molar ratio on the crystallite size, morphology, lattice parameter, and chemical composition of the prepared ZnGa₂O₄ spinel particles were investigated. The diffusion of Zn²⁺ ions seemed to be the key for the synthesis and growth of the spinel, especially for the achievement of a stoichiometric composition. With increasing ZnO/Ga₂O₃ molar ratio and treatment temperature, the synthesized spinel particles increased in size and their composition approached stoichiometric. ZnGa₂O₄ spinel particles with the composition ZnO/Ga₂O₃=1 were synthesized from the relatively concentrated solutions, *e.g.*, 0.2 mol dm⁻³ Ga₂(SO₄)₃ and at ZnO/Ga₂O₃=1.95, under hydrothermal conditions at 240 °C for 50 h.

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