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Direct Precipitation of Spinel-Type Zn(Fe, Ga)$_2$O$_4$ Solid Solutions from Aqueous Solutions at 90°C: Influence of Iron Valence of Starting Salt on Their Crystallite Growth

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Spinel-type solid solutions in the whole range of compositions between $ZnGa_2O_4$ and $ZnFe_2O_4$ were directly precipitated as nanoparticles by dropping the starting mixed solutions of zinc sulfate, gallium sulfate, and either divalent iron chloride or trivalent iron nitrate into aqueous ammonia at 90°C. Direct precipitation of nanosized spinel-type Zn(Ga,Fe)O$_4$ solid solutions was also achieved by aging the mixed solutions in the presence of either urea or hexamethylenetetramine at 90°C except for one case (i.e., aging the solutions using trivalent iron salt in the presence of urea). With increased iron content in the spinel-type solid solution precipitates, their crystallite size decreased when trivalent iron salt was used, but increased when divalent iron salt was used. Change of lattice parameter a_0 of the spinel-type solid solutions was confirmed to follow the Vegard's Law.

Key Words: **spinel; $ZnGa_2O_4$; $ZnFe_2O_4$; solid solution; nanometer-sized particle.**

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1. INTRODUCTION

$ZnGa_2O_4$ with spinel-type structure is UV-transparent and electroconductive so that it has a possibility to be utilized for UV-photoelectronic devices as one of the new transparent and conductive materials (1–3), as well as a good low-voltage phosphor material used in a new kind of vacuum flat cathode ray tube of the field emission display (4). Synthesis of reactive fine powders of $ZnGa_2O_4$ spinel through chemical solution routes, i.e., glycothermal synthesis at 300°C (5) and hydrothermal synthesis below 240°C (6–8) have been reported. In our previous paper (9), ultrafine $ZnGa_2O_4$ particles have been successfully precipitated under normal pressure either by dropping a mixed solution of zinc sulfate and gallium sulfate into aqueous NH_3 at a temperature of 25 – 90°C with stirring or by aging the mixed solution in the presence of urea or hexamethylenetetramine (HMT) at 90°C. For zinc ferrite $ZnFe_2O_4$, successful synthesis has been reported from the aqueous solution of respective metal chlorides at a temperature between 30°C and 60°C through hydrolysis by either ammonia or hydrazine under normal pressure (10, 11). However, there is little data on direct synthesis of solid solutions between these two spinels, $ZnGa_2O_4$ and $ZnFe_2O_4$.

We have found a phenomenon that the crystallite sizes of hydrothermally precipitated CeO_2 (12) and Gd-doped CeO_2 through homogeneous precipitation using HMT (13) have been greatly affected by valence of using cerium salts (i.e., whether trivalent or tetravalent cerium salts). In the present study, fine particles of Zn(Ga, Fe)$_2$O$_4$ solid solutions with spinel-type structure have been successfully obtained by direct precipitation from aqueous solutions at 90°C. The influences of valence of iron in its starting salt on the particle morphology and crystallite size of the resulting solid solutions have been investigated.

2. EXPERIMENTAL

Reagent grades of zinc sulfate ($ZnSO_4 \cdot 7H_2O$), gallium sulfate ($Ga_2(SO_4)_3 \cdot 16H_2O$), Fe(II) chloride ($FeCl_2 \cdot 4H_2O$), and Fe(III) nitrate ($Fe(NO_3)_3$) with high purity, more than 99.9%, were employed as starting metal salts. The starting mixed solutions were prepared by dissolving zinc sulfate, gallium sulfate and either Fe(II) chloride or Fe(III) nitrate to obtain a metal atom ratio of $Zn/(Ga + Fe) = \frac{1}{2}$ into distilled water in different concentrations. Three hydrolysis agents were used for the preparation of solid solutions Zn(Ga,Fe)$_2$O$_4$; reagent grades of aqueous ammonia, urea ($CO(NH_2)_2$, and hexamethylenetetramine (HMT, $(CH_2)_6N_4$) (hereafter aq.-NH_3, urea, and HMT method, respectively).

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In the aq.-NH_3 method, the starting mixed solution with a metal concentration of Zn $= 0.018\,\text{mol}\,\text{dm}^{-3}$ and Ga + Fe $= 0.036\,\text{mol}\,\text{dm}^{-3}$ in different Ga/Fe ratios (i.e., $\text{Zn}/(\text{Ga}+\text{Fe}) = \frac{1}{2}$) was added directly to a $0.09\,\text{mol}\,\text{dm}^{-3}$ aqueous NH_3 at 90°C with stirring for 20 h. In the urea and HMT methods, urea solution with a concentration of $0.32\,\text{mol}\,\text{dm}^{-3}$ and HMT solution with $0.16\,\text{mol}\,\text{dm}^{-3}$ were mixed into the same starting solution, respectively, and then heated to 90°C with stirring for 20 h to effect precipitation. The precipitates obtained were separated by centrifuging, washed with distilled water, and then dried in an oven at 60°C in air. The powders obtained were gently crashed in order to be deagglomerated.

Crystalline phase in the as-prepared precipitates after dried at 60°C was identified using X-ray powder diffractometry (XRD) with Cu$K\alpha$ radiation. The crystallite size was calculated from line broadening of the 400 diffraction line of spinel structure according to the Scherrer equation. The lattice parameter of the spinel was measured using silicon as an internal standard. The samples after annealing at 600°C in air for 1 h were used for the lattice parameter measurement. The morphology and size of the precipitates were observed using transmission electron microscopy (TEM).

3. RESULTS

3.1. *Aq.-NH_3 Method*

XRD profiles of as-prepared precipitates after dried at 60°C, that were obtained by the reaction at 90°C for 20 h using Fe(II) and Fe(III) salts, are shown in Figs. 1 and 2, respectively. All samples showed to have cubic spinel structure in a single phase. However, there was a difference in the broadness of diffraction lines; spinel crystals derived from Fe(III) salt had broader diffraction lines than those from Fe(II) salt. In Fig. 3, crystallite size of as-prepared precipitates after dried at 60°C, that were calculated from 400 diffraction line of spinel, is plotted against the content of iron in solid solutions. It revealed a clear difference in crystallite size of spinel solid solutions derived from iron ions with different initial valence, i.e., the crystallite size increased with the increase in Fe^{2+} content, but decreased with the increase in Fe^{3+} content.

Changes in the morphology and particle size of as-prepared spinel precipitates are shown in Fig. 4 via TEM micrographs. It was clearly observed that the primary particles of spinel formed from Fe(II) salt were coarser than those from Fe(III) salt. In the samples obtained from Fe(II) salt, the particle size of the sample with $\text{Fe}/\text{Ga} = \frac{10}{0}$ appeared to be larger than that with $\text{Fe}/\text{Ga} = \frac{5}{5}$. In the samples obtained from Fe(III) salt, on the other hand, the change in crystallite size with Fe content was reversed. The TEM observation showed relatively good correspondence with the data obtained by XRD line broadening (Fig. 3).

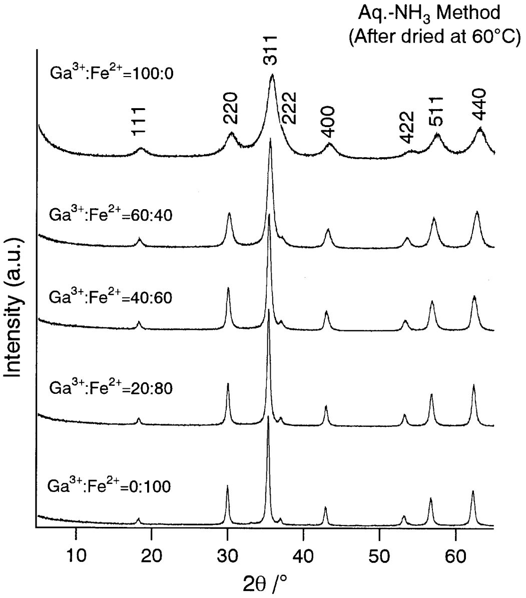

FIG. 1. XRD patterns of precipitates formed at the starting compositions (molar ratio) of Ga:Fe = 100:0, 60:40, 40:60, 20:80, and 0:100 from the mixed solutions using $ZnSO_4$, $Ga_2(SO_4)_3$, and $FeCl_2$ by aq.-NH_3 method at 90°C.

The lattice parameter, a_0, of the spinel samples was measured after heat treatment at 600°C, because diffraction lines of as-precipitated solid solutions were broad.

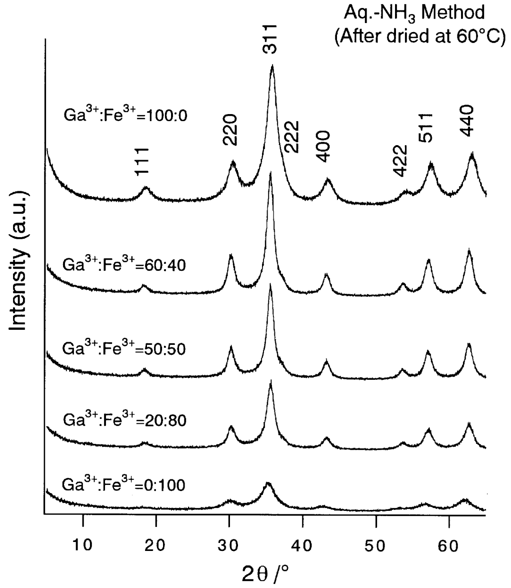

FIG. 2. XRD patterns of precipitates formed at the starting compositions (molar ratio) of Ga:Fe = 100:0, 60:40, 50:50, 20:80, and 0:100 from the mixed solutions using $ZnSO_4$, $Ga_2(SO_4)_3$, and $Fe(NO_3)_3$ by aq.-NH_3 method at 90°C.

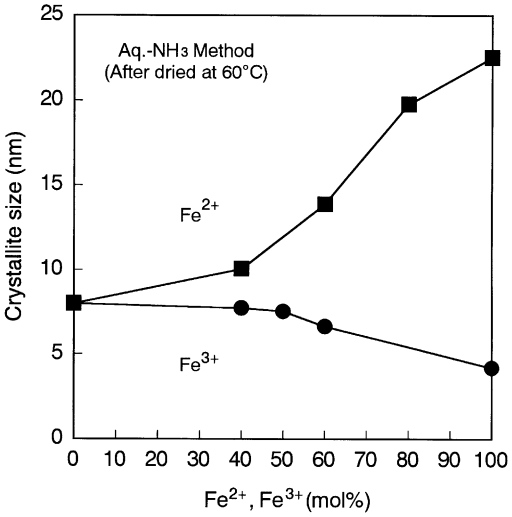

FIG. 3. Crystallite size of $Zn(Fe,Ga)_2O_4$ spinel particles prepared by aq.-NH_3 method at 90°C as a function of molar ratio (mol%) of (Fe^{2+} or Fe^{3+})/(Fe + Ga) in the starting mixed solution.

Change in the lattice constant, a_0, of the solid solutions is shown in Fig. 5 against the content of iron. The lattice parameter was proved to linearly increase with increasing iron content according to Vegard's Law, irrespective of the valence state of the starting iron ions (whether divalent or trivalent). The measured lattice parameters for the end members $ZnGa_2O_4$ and $ZnFe_2O_4$ showed good coincidence with published data (14, 15) as shown by the open circles in the figure. It was confirmed that the solid solutions between $ZnGa_2O_4$ and $ZnFe_2O_4$ in overall compositions could be directly synthesized.

3.2. *Urea and HMT Method*

XRD patterns of precipitates after dried at 60°C, that were obtained from mixed solutions of divalent or trivalent iron, gallium, and zinc salt using HMT and urea method at 90°C for 20 h are shown in Figs. 6 and 7, respectively. When divalent iron salt ($FeCl_2$) was used, direct precipita-

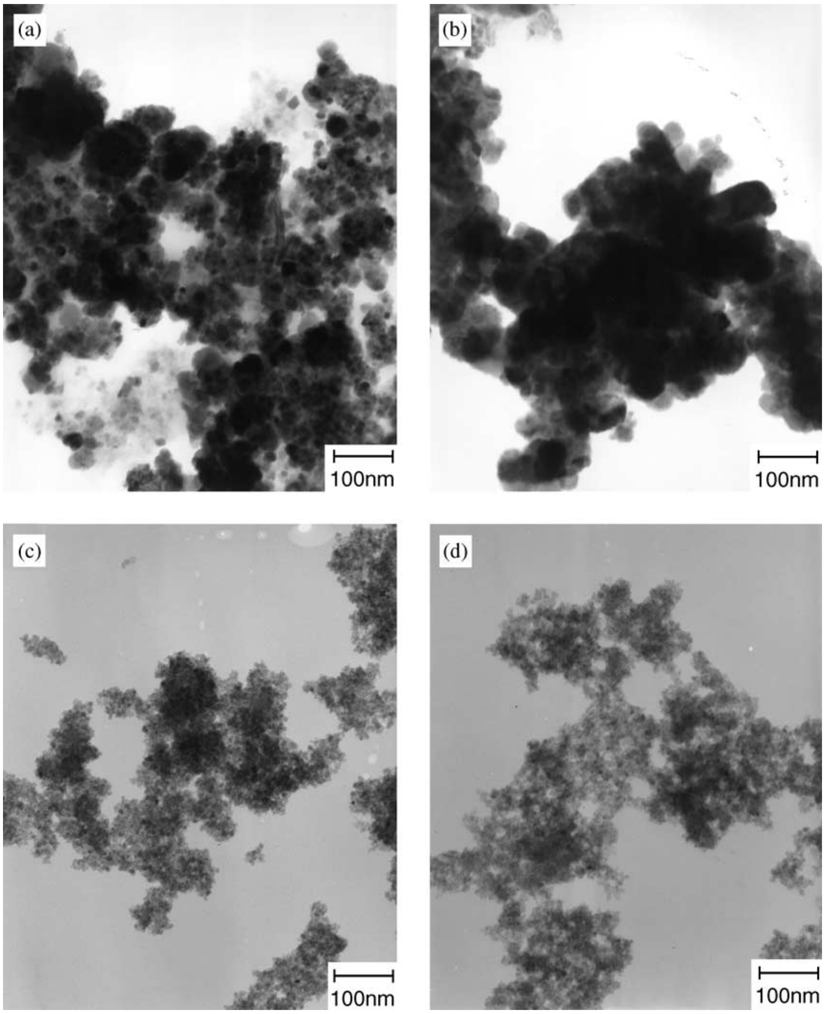

FIG. 4. TEM micrographs of $Zn(Fe,Ga)_2O_4$ spinel particles prepared by aq.-NH_3 method at 90°C; (a) Ga^{3+} : Fe^{2+} = 50:50, (b) Ga^{3+}:Fe^{2+} = 0:100, (c) Ga^{3+}:Fe^{3+} = 50:50, and (d) Ga^{3+}:Fe^{3+} = 0:100.

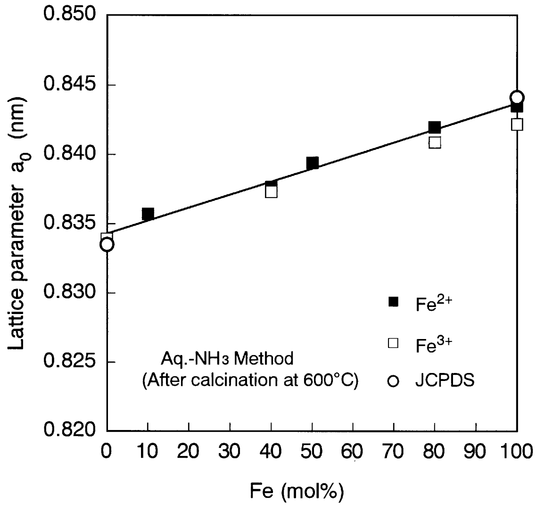

FIG. 5. Lattice parameter, a_0, of Zn(Fe,Ga)$_2$O$_4$ spinel particles prepared by aq.-NH$_3$ method at 90°C versus molar ratio (mol%) of Fe/(Fe + Ga).

tion of nanosized spinel-type Zn(Ga,Fe)O$_4$ solid solutions was achieved via HMT and urea method. When trivalent iron salt (Fe(NO$_3$)$_3$) was used, direct precipitation of nanosized spinel-type Zn(Ga,Fe)O$_4$ solid solutions was directly formed through HMT method (Fig. 6b), although spinel-type solid solutions were not prepared through urea method under the present conditions and basic zinc salt and α-FeO(OH) and/or α-GaO(OH) phase appeared (Fig. 7b). With increased Fe^{2+} content in the spinel-type solid solutions precipitated, diffraction lines became sharp as compared with the cases obtained from trivalent iron salt (Fig. 6b), which suggests that their crystallite size increased in both cases (Figs. 6a and 7a) similar to aq.-NH$_3$ method.

4. DISCUSSION

Concerning low-temperature synthesis of related spinel compounds, ZnAl$_2$O$_4$ has been reported to be synthesized at 550°C by the polyvinyl alcohol evaporation route (16), and ZnCr$_2$O$_4$ at around 500°C by coprecipitation from solutions of acetate precursors with tetraethyl ammonium hydroxide (17). Hydrothermal synthesis below 240°C could offer direct route to single phase of ZnGa$_2$O$_4$ spinel with high crystallinity (6–8). Three precipitation methods for direct synthesis of nanosized ZnGa$_2$O$_4$ spinel at 25 – 90°C have been also presented (9). When aqueous ammonia was added into trivalent gallium and divalent zinc sulfate solution separately, gallium hydroxide (GaO(OH)) and zinc oxide were precipitated as main product, respectively (18). From divalent iron salt solution, Fe(OH)$_2$ precipitates have been formed by the addition of aqueous ammonia, and α-FeOOH, β-FeOOH, and α-Fe$_2$O$_3$ have been obtained from Fe(OH)$_2$ precipitates (19). Both ZnGa$_2$O$_4$ and ZnFe$_2$O$_4$ are normal spinel, and the solid solutions at whole composition range in ZnGa$_2$O$_4$–ZnFe$_2$O$_4$ system were achieved as direct precipitation from aqueous mixed solutions at 90°C by aging for 20 h under normal pressure through chemical solution route in the present study. In order to get single phase of spinel avoiding local and separated precipitation of individual metal ions, the

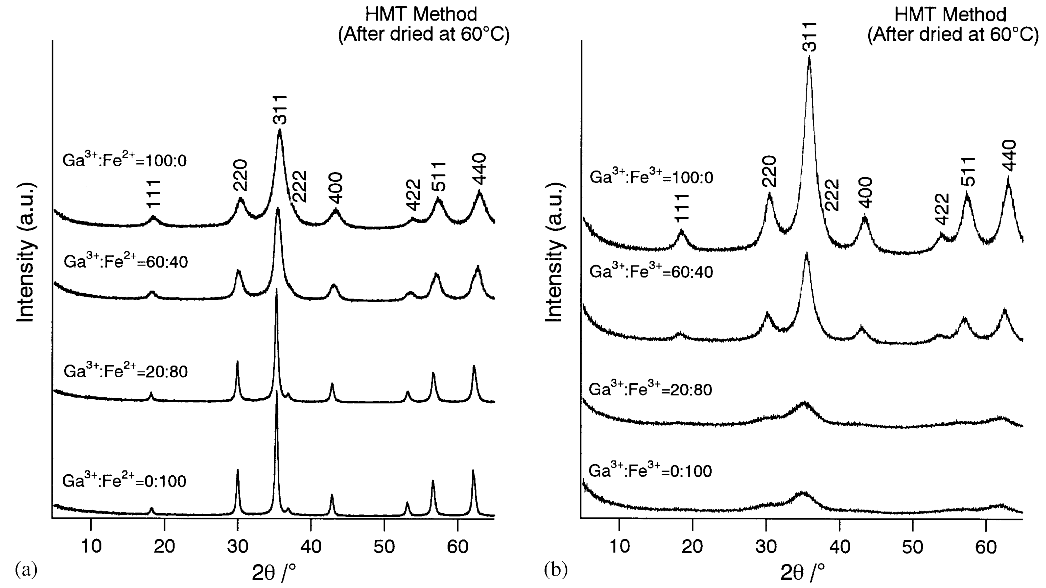

FIG. 6. XRD patterns of precipitates prepared at the starting compositions of Ga:Fe = 100:0, 60:40, 20:80, and 0:100 from the mixed solutions using (a) ZnSO$_4$, Ga$_2$(SO$_4$)$_3$, and FeCl$_2$ and (b) ZnSO$_4$, Ga$_2$(SO$_4$)$_3$, and Fe(NO$_3$)$_3$ by precipitation using HMT at 90°C.

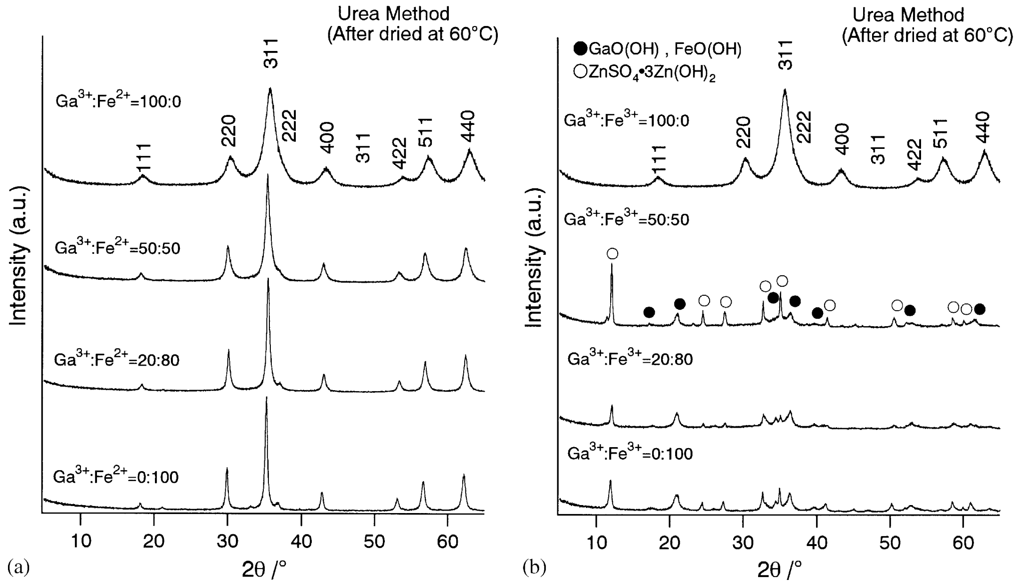

FIG. 7. XRD patterns of precipitates prepared at the starting compositions of Ga:Fe = 100:0, 50:50, 20:80, and 0:100 from the mixed solutions using (a) $ZnSO_4$, $Ga_2(SO_4)_3$, and $FeCl_2$ and (b) $ZnSO_4$, $Ga_2(SO_4)_3$, and $Fe(NO_3)_3$ by precipitation using urea at 90°C.

starting mixed solution was essential to be added as small droplets into an excess amount of aqueous ammonia solution heated with stirring.

Reaction temperature and time are important factors influencing the composition and structure of the precipitates obtained through the soft solution routes. $ZnGa_2O_4$ particles have been reported to be successfully precipitated under normal pressure either by dropping a mixed solution of zinc sulfate and gallium sulfate into aqueous NH_3 at a temperature of 25 – 90°C with stirring or by aging the mixed solution in the presence of urea or HMT at 90°C (9). It was shown that aging at a temperature above 30°C for more than 2 h was required in order to obtain spinel-type crystalline $ZnFe_2O$ from the mixed solution of $ZnCl_2$ and $FeCl_2$ via addition of aq. NH_3, (10) because the so-called green-rust phase (19, 20) containing both Fe^{3+} and Fe^{2+} ions and anions (OH^- and Cl^-) was formed at the early time of aging, i.e., 0.5–1 h (10). In the present study, spinel-type crystalline $ZnFe_2O$ was formed from the solution of $ZnSO_4$ and $FeCl_2$ after aging for 20 h at 90°C via the aq,-NH_3 method, and the green-rust phase was not observed because reaction temperature was high (90°C) and time of aging was long (20 h). These results coincided with those reported (10). When $FeCl_3$ instead of $FeCl_2$ was used as the starting material to prepare the starting solution, amorphous phase was reported to be obtained after reaction at 60°C for 8 h (10). In the present study, nanometer-sized minute particles having spinel-type structure of $ZnFe_2O$ were obtained via the aq,-NH_3 method after reaction at higher temperature (90°C) and longer reaction time (20 h) than those reported. Although particles formed after reaction at 60°C for 8 h were very minute and could not be detected as crystalline spinel (10), it seems to have grown to nanometer-sized minute particles detectable as spinel-type structure of $ZnFe_2O$ through crystallite growth by aging for long period of time (20 h) at high temperature (90°C) as shown in Fig. 2.

Basic zinc carbonate (21) and zinc oxide (22) were reported to be formed from zinc sulfate solution through homogeneous precipitation technique using urea and HMT, respectively. Basic zinc sulfate was reported to be formed from zinc sulfate solution through slow addition of aqueous ammonia under stirring (23). Spinel-type $Zn(Fe,Ga)_2O_4$ solid solutions were not formed only in one case in this study. Basic zinc sulfate and α-FeO(OH) (goethite) and/or α-GaO(OH) (supposedly making solid solutions between α-FeO(OH) and α-GaO(OH)) were formed through urea method only using Fe(III) salt (Fig. 7b). Fe(III) cations tend to make precipitation of $Fe(OH)_3$ under acidic conditions at low pH near 1–2 and $Fe(OH)_3$ dehydrates spontaneously to form α-FeO(OH) (goethite), but Fe(II) cations and Zn(II) cations are precipitated as hydroxide and/or oxide under more neutral conditions at similar pH $\sim$7 than Fe(III) cations. Combination of Fe(II) cations, Ga(III) cations, and Zn(II) cations are considered to be more easily apt to make coprecipitates than that of Fe(III) cations, Ga(III) cations, and Zn(II) cations. It seems that urea concentration used in the present study might be a little low and was lacking for direct formation of spinel-type $Zn(Fe,Ga)_2O_4$ solid solutions in the case of urea method using Fe(III) salt.

A phenomenon; particles obtained from tetravalent cerium salt had a very fine crystallite size, which was very distinct from the particles prepared from the trivalent cerium salt having large crystallite size, was reported to be observed in both cases of preparation of pure CeO_2 through hydrothermal treatment in the presence of aqueous ammonia (12) and Gd-doped CeO_2 via homogeneous precipitation in the presence of HMT (13). The nucleation number mainly governs the size of the synthesized particles. In the preceding case, because of the necessity of Ce^{3+} to be oxidized to Ce^{4+} in the solution, the rate and the number of nucleation of the hydroxide from the trivalent cerium salt may be slower and fewer than those from the tetravalent cerium salt where no valence change occurs. When the degree of supersaturation for nucleation was low, micrometer-sized particles grew from the trivalent cerium salt solution (24), in contrast with nanometer-sized particles from tetravalent cerium salt solution (25) through thermal hydrolysis of acidic solutions under hydrothermal conditions. In the present study, the same phenomenon is supposed to be observed. With increasing Fe content, the crystallite size of the solid solutions prepared from Fe^{2+} salt increased, but that from Fe^{3+} salt decreased, as shown in Fig. 3. It seems to be reasonable as one of the tried explanations that this phenomenon has resulted from the difference in nucleation number. This result suggests that the nucleation number in the solution containing Fe^{2+} salt must be much less than that containing Fe^{3+} salt. The degree of supersaturation for nucleation must be much lower because oxidation of Fe^{2+} to Fe^{3+} in the solution, which is necessary to occur for the formation of $ZnFe_2O_4$, is supposed to require time to occur.

5. SUMMARY

Spinel-type solid solutions in overall composition between $ZnGa_2O_4$ and $ZnFe_2O_4$ were directly synthesized through the three chemical solution routes, i.e., (i) by dropping a mixed solution of zinc, gallium, and either divalent iron or trivalent iron salts into aqueous ammonia and by aging the mixed solutions in the presence of either (ii) urea or (iii) HMT at 90°C except for one case (i.e., aging the solutions using trivalent iron salt in the presence of urea). The crystallite size of the spinel particles clearly showed composition dependence and reverse tendency between starting divalent iron and trivalent iron salts used. This phenomenon was explained by the difference in nucleation number because of low supersaturation degree based on the necessity of occurrence of oxidation of Fe^{2+} to Fe^{3+} in the divalent iron salt solution.

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