Chemical synthesis of crystalline, pure or Mn-doped $ZnGa_2O_4$ powders at 90 °C

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Crystalline, pure or Mn-doped $ZnGa_2O_4$ powders have been prepared *in situ* in urea (with or without enzyme urease)-containing Zn and Ga nitrate (and Mn nitrate) solutions by simply holding those for 24–48 h, at 90 °C, in screw-capped glass bottles in a constant-temperature laboratory oven. Single-phase pure or Mn-doped zinc gallate powders synthesized with the spinel crystal structure had an average particle size around 15 to 18 nm. Powders were characterized by x-ray diffraction, scanning electron microscopy, energy-dispersive x-ray spectroscopy, inductively-coupled plasma atomic emission spectroscopy, simultaneous thermogravimetry and differential thermal analysis, Fourier-transformed infrared spectroscopy, and carbon and nitrogen analyses. Calcination behavior of the as-filtered powders was later studied in an air atmosphere over the temperature range of 90 to 1200 °C.

I. INTRODUCTION

The phenomenon of electroluminescence (EL)[1] can be described as the nonthermal conversion of electrical energy into luminous energy. In EL devices, light is generated by impact excitation of a light emitting center present in the material by high-energy electrons, which gain their high energy from an electric field. In general, phosphors, whether being used for EL or cathode ray tubes (CRTs), consist of a host material doped with, e.g., Mn atoms for the light emission centers. To be a phosphor host lattice, a material must satisfy the basic condition of having a band gap large enough to emit visible light without absorption.[1] This narrows the choice of possible materials down to large band-gap semiconductors ($E_g > 2.5$ eV) and insulators.

Sulfide phosphors have been in widespread use in CRTs and vacuum fluorescent displays (VFDs). However, sulfide-based phosphors release sulfide gases during electron excitation, subsequently causing the cathode filament to deteriorate and the luminance efficiency of phosphors to decrease as well. $ZnGa_2O_4$ (zinc gallate) powder phosphor has been studied[2] as an alternative of the blue cathodoluminescent phosphor of ZnS:Cl. $ZnGa_2O_4$ of spinel structure has a band gap of 4.4 eV and gives emission from green to red when it is doped with Cr and Mn. It shows blue emission even in its pristine form.[3] Therefore, $ZnGa_2O_4$ has been considered[4,5] as an excellent material for multicolor emitting thin-film EL (TFEL) devices.

The preferred route of preparation for pure or doped $ZnGa_2O_4$ ceramic phosphors has been the solid-state reactive firing (SSRF) of the appropriate amounts of ZnO and Ga_2O_3 powders.[2–5] Nevertheless, this old technique of ceramic manufacture required temperatures well above 1000 °C (for prolonged firing times typically in the vicinity of 24 h) to form the single-phase, spinel phosphor. Since the volatilization of Zn at high temperatures (owing to its high vapor pressure) is a serious problem, a practical way of synthesizing $ZnGa_2O_4$ at lower temperatures is strongly needed.

Wet chemical methods have been tested for the synthesis of $ZnGa_2O_4$ by several researchers.[6–10] Aqueous mixing of GaO(OH) and Zn oxalate precursors[6] required calcination at around 700 °C for obtaining single-phase $ZnGa_2O_4$. Hsu *et al.*[7] added Ga_2O_3 powders into an alcoholic solution stirred at 75 °C, containing dissolved zinc nitrate and urea, to coat the surfaces of Ga_2O_3 particles with ZnO after 5 to 15 h of wet-mixing, and the obtained precursors calcined at 1100 °C still consisted of two-phase mixtures of $ZnGa_2O_4$ and smaller amounts of either ZnO or Ga_2O_3. Hydrothermal synthesis has also been studied[8,9] for the manufacture of $ZnGa_2O_4$ powders. Li *et al.*[8] placed $GaCl_3$ solutions and elemental Zn powders in an autoclave at 150–170 °C for 10 h. Hirano *et al.*[9] on the other hand, used Zn and Ga sulfates as the starting materials and studied the influence of autoclave

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temperature and reaction time on the phase purity of products. Beauger *et al.*[10] used thermogravimetry for synthesizing pure and Mn-doped $ZnGa_2O_4$ ceramics, starting with a mixture of nitrate salts of all the elements involved.

This work presents results of experiments leading to a successful synthesis of single-phase, nano-sized and crystalline pure or Mn-doped $ZnGa_2O_4$ powders at 90 °C, following 24 to 48 h aging of clear, aqueous solutions of urea/enzyme urease and Zn and Ga (and Mn) nitrates simply held in screw-capped ordinary glass bottles in a laboratory oven. Postsynthesis calcination behavior of the as-filtered $ZnGa_2O_4$ powders is also presented.

II. EXPERIMENTAL PROCEDURE

$Ga(NO_3)_3 \cdot 4.06H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, and a manganese nitrate solution (ICP/DCP standard) were used in the synthesis. The 0.3704 M Ga^{3+} and 0.7404 M Zn^{2+} stock solutions were prepared by dissolving the stoichiometric amounts of Ga and Zn nitrate salts in deionized water. Urea (H_2NCONH_2) used was of reagent grade, and the enzyme urease used had a concentration of 5 units/mg.

Appropriate amounts of the stock solutions were added to approximately 90 ml of deionized water. The solution was mixed at RT (room temperature) for about 5 min, and then urea powder was added to this solution, followed by 5 min of stirring at RT. Urea additions have been tested (i.e., runs 1 through 7 in Table I) over the range of 2.00 ($= 0.0333$ mol) to 5.50 g ($= 0.0916$ mol). The molar ratio of urea-to-cations (U/C), therefore, has only been varied over the interval of 9.25 and 25.4. Following the dissolution of urea powder (and enzyme urease, in some experiments) in the cation solution, the clear liquid was immediately transferred into a capped glass bottle and then placed into a laboratory oven kept at 90 ± 0.5 °C.

In the synthesis of Mn-doped $ZnGa_2O_4$ powders, a 6.5-ml aliquot (i.e., 0.0024 mol of Ga^{3+}) of the Ga^{3+} stock, 1.61 ml (i.e., 0.00119 mol of Zn^{2+}) of Zn^{2+} stock, and 0.04 ml of Mn solution were mixed with 89 ml of deionized water (i.e., run 8 in Table I). In a similar fashion, an increased level of Mn-doping in $ZnGa_2O_4$ has been studied in run 9 of the same table. A 5.5-g amount of urea was then added to these solutions, followed by 10 min of stirring at RT. U/C correspond to 25.4 in both cases. Solutions of this study were aged at 90 °C for 24 to 72 h.

Precipitates were separated from their mother liquors by centrifugal filtration (5000 rpm), followed by washing 3× with 2-propanol (>99%, Merck). Washed precipitates were dried in an oven at 90 °C, overnight. Dried powders were ground by hand in an agate mortar and then isothermally calcined, as loose powder stacks, in alumina boats, in a stagnant air atmosphere at various temperatures in the range of 250 to 1000 °C. Each calcination batch was heated to the specified temperature at the rate of 5 °C/min, soaked at this temperature for 6 h and then cooled back to room temperature at the same rate.

The phase constitution of the powders was analyzed as a function of calcination temperature by a powder x-ray diffractometer (D-5000, Siemens GmbH, Karlsruhe, Germany) using Cu K_α radiation (40 kV, 30 mA, step size 0.016°, count time 1 s, 10–135° in 2θ). A silicon external standard to correct for systematic errors was used, along with the Appleman least-squares refinement program,[11] for precisely determining the lattice parameters.

Pyrolysis of the powders was monitored by simultaneous differential thermal and thermogravimetric analysis (STA501, Bähr GmbH, Bremen, Germany) in air at a scan rate of 5 °C/min up to 1080 °C. Infrared transmittance plots of powder samples were recorded from Fourier transform infrared (FTIR) (IFS 66, Bruker GmbH, Karlsruhe, Germany) pellets, pressed after mixing the powder samples (1 wt%) with dry KBr. The residual C and N contents of powders were determined by the combustion-IR absorption method (CS-800, Eltra

TABLE I. Critical parameters of powder synthesis experiments.

Run	Ga (ml)	Zn (ml)	Mn (ml)	H_2O (ml)	Urea (g)	Urease (g)	U/C (M)	Temp. (°C)	Time (h)	Phases and percentages (runs 2 to 4)
0	6.5	⋯	⋯	90	1.333	⋯	9.25	90	3	α-GaOOH
1	6.5	1.62	⋯	89	2.0	⋯	9.25	90	3	α-GaOOH
2	6.5	1.62	⋯	89	2.0	⋯	9.25	90	24	α-GaOOH + $ZnGa_2O_4$ (35% + 65%)
3	6.5	1.62	⋯	89	2.0	⋯	9.25	90	72	α-GaOOH + $ZnGa_2O_4$ (20% + 80%)
4	6.5	1.62	⋯	89	5.5	⋯	25.4	90	24	α-GaOOH + $ZnGa_2O_4$ (15% + 85%)
5	6.5	1.62	⋯	89	5.5	⋯	25.4	90	48	$ZnGa_2O_4$
6	6.5	1.62	⋯	89	5.5	0.5	25.4	90	24	$ZnGa_2O_4$
7	6.5	1.62	⋯	89	5.5	⋯	25.4	120	24	$ZnGa_2O_4$
8	6.5	1.61	0.04	89	5.5	⋯	25.4	90	48	$ZnGa_2O_4$
9	6.5	1.46	0.66	88	5.5	⋯	25.4	90	48	$ZnGa_2O_4$
10	6.5	1.46	0.66	88	5.5	⋯	25.4	120	24	$ZnGa_2O_4$

GmbH, Neuss, Germany). Morphology and chemical composition of the zinc gallate powders were studied by field-emission scanning electron microscopy (FESEM) (DSM-982 Gemini, Zeiss GmbH, Oberkochen, Germany) and quantitative energy-dispersive spectroscopy (EDS) (6103, Oxford Microanalysis Group, Oxford, U.K.) after calibration with a cobalt standard, respectively. The chemical analyses of the Mn-doped $ZnGa_2O_4$ samples were performed by using inductively-coupled plasma atomic emission spectroscopy (ICP-AES, JY-70Plus, Jobin Yvon S.A., Longjumeau, France).

III. RESULTS AND DISCUSSION

Formation of a solid precursor in aqueous precipitation experiments, which specifically employ the homogeneous decomposition of urea[12–15] is governed by the

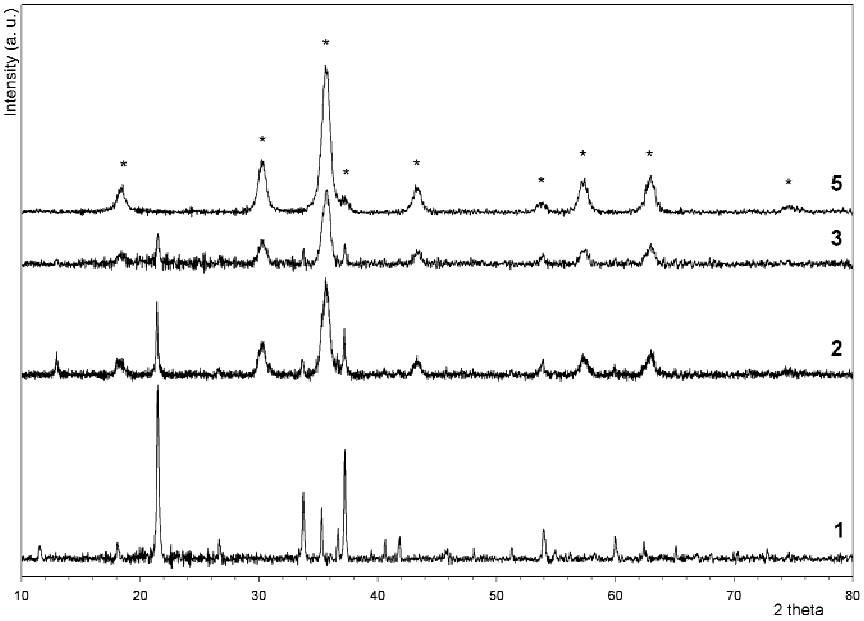

FIG. 1. XRD traces of precipitates obtained (following drying at 90 °C) from runs 1, 2, 3, and 5 of Table I, where the legends designate the run numbers and an asterisk indicates the spinel peaks.

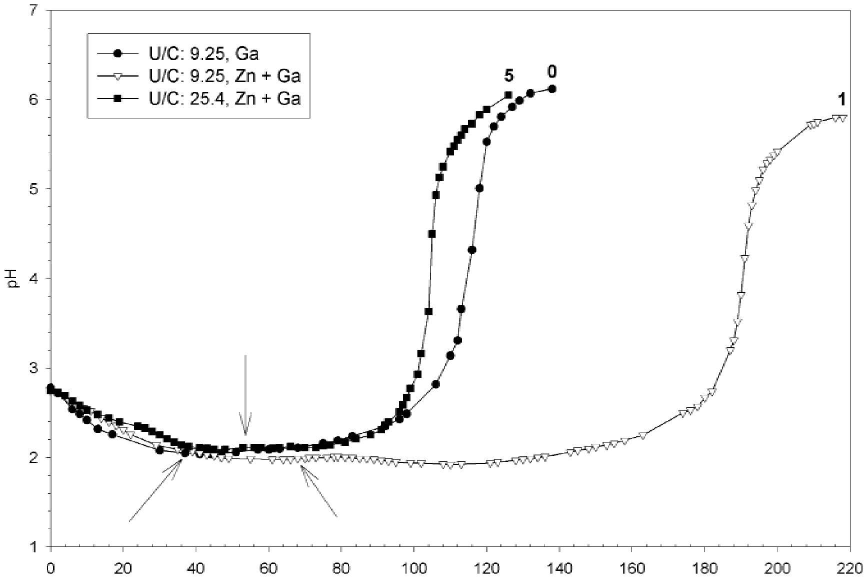

FIG. 2. Superimposed pH–time plots of runs 0, 1, and 5 of Table I. Solutions were slowly heated in covered glass beakers on a hot-plate from RT (i.e., $t = 0$) to 90 °C (i.e., $t = 45$ min).

controlled and smooth generation of hydroxide and carbonate ions. The kinetics of the decomposition of urea in water[13,14] depends on its concentration, as well as other important variables, such as temperature and the presence and concentration of supporting ions. This paper unfortunately excludes the detailed examination of possible effects of cation(s) concentration and, to a certain extent, of aging temperature on the morphology of the resultant powders.

A summary of solution preparation procedures of this work[16] is given in Table I. The phases observed (via XRD) in the powders recovered from the glass bottles (directly after drying at 90 °C, overnight) are presented in the last column of this table. Figure 1 shows the XRD traces of the powders recovered from runs 1, 2, 3, and 5 of Table I. The only crystalline phase present in run-1 samples was α–GaOOH, which was found to have an orthorhombic unit cell with the lattice parameters a = 4.561(3), b = 9.798(3), and c = 2.973(2) Å. It is obvious from the XRD data of Fig. 1 that only with an increase in aging time (runs 1 through 3) from 3 to 24 h (at 90 °C), it is possible to form the $ZnGa_2O_4$ spinel. In runs 2 and 3 the major phase was the $ZnGa_2O_4$ spinel.

In the early stages of the precipitation process, which take place in urea, Zn^{2+}- and Ga^{3+}-containing solutions were monitored (in a 150-ml-capacity beaker) as a function of aging time and pH. The solution temperature was explicitly increased from 23 to 90 °C in about 45 min (on a hot plate) for these pH determination experiments, unlike the standard experiments in which the solutions in sealed glass bottles were immediately placed in a laboratory oven kept constantly at 90 ± 0.5 °C. Temperatures in the standard experiments were simply deduced from the global temperature of the oven. A typical plot of pH versus time is given in Fig. 2. The trace of pH variation with time for solutions only containing Ga^{3+} ions (0.0024 mol of Ga^{3+} and 0.0222 mol of urea, i.e., run 0) is also included in Fig. 2 for the purpose of direct comparison. The interesting ellipsoidal morphology possessed by the α–GaOOH crystals initially formed in run-0 solutions has been depicted in Fig. 3(a). The numbers over the traces of Fig. 2 denote the run numbers from Table I, while the arrows indicate the starting points for ellipsoidal GaOOH precipitation.

The initial pH value of all solutions (of Fig. 2) was around 2.75 (at 23 °C and t = 0), and the precipitation started (by the onset of a slight turbidity) when the pH dropped, with a smooth increase in the solution temperature, to about 2.0 to 2.1 (at $\geqslant$85 °C). It is interesting to note that the urea itself does not directly impact precipitation but rather its decomposition products and change in pH do so, consistent with results reported elsewhere.[17] For solution chemistries identical to run 1 and 5, short reaction periods, such as $\leqslant$3 h resulted in the precipitation of ellipsoidal GaOOH. Figure 3(b) shows the final morphology of α–GaOOH precipitates (run 0) after 24 h of aging in their mother liquors. The abrupt rise observed in pH (when t > 90 min) in all solutions was typical[15] for the decomposition of urea, and it corresponded to the rapid dissociation of NH_4OH (which is an initial byproduct of urea decomposition together with H_2CO_3) into NH^{4+} and OH^-. The detailed sequence of chemical reactions describing the decomposition of urea in aqueous media has previously been documented.[13,14]

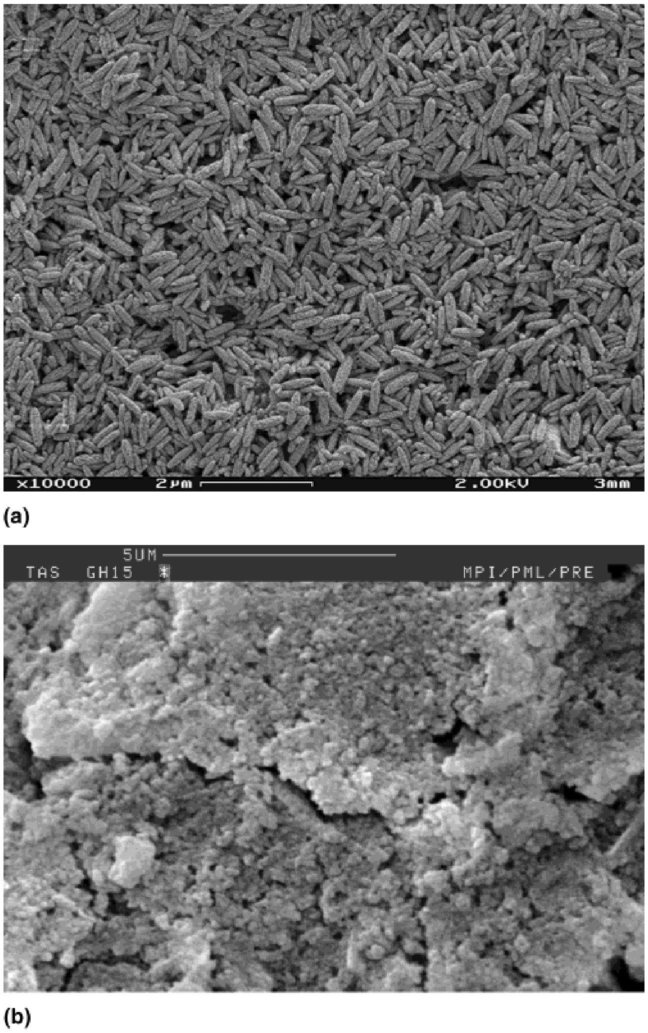

FIG. 3. SEM micrograph of (a) ellipsoidal α–GaO(OH) crystals recovered from run-0 (Table I) solutions at the 40th minute of heating (pH = 2 at 85 °C) and (b) precipitate powder obtained after 24 h of aging (pH approximately 8 at 90 °C).

When the U/C was equal to 9.25 (i.e., runs 1 to 3), the presence of Zn^{2+} ions in the solutions was observed to have a strong effect in delaying the start of precipitation (indicated by arrows in Fig. 2). For the same U/C ratio (i.e., 9.25, in Fig. 2), pure Ga^{3+} solutions started earlier (38th minute) to precipitate GaO(OH) ellipsoidal particles [see Fig. 3(a)] at a pH value in the vicinity of 2 (at approximately 84 °C). When Zn^{2+} ions were also present in the solution (Fig. 2, run 1), the incubation time required for the start of precipitation increased to around 70 min. Meanwhile, increasing the U/C (to 25.4, run 5) resulted in a decrease in the incubation time. Solutions used in run 5 samples were able to produce single-phase $ZnGa_2O_4$ after 48 h of aging at 90 °C, while the same solutions aged at 90 °C for only 24 h produced a two-phase mixture of $ZnGa_2O_4$ and GaOOH. pH values of all solutions of Fig. 2 increased from around 6 (after 2–3 h of aging) to 7.8 or 8.9, the final value being a strong function of the initial concentration of urea, after aging (24–48 h) at 90 °C.

Hirano *et al.*[9] had observed the formation of GaO(OH) crystals in the product powders they filtered out after keeping their hydrothermally treated solutions, in an autoclave, at 100 °C for about 20–50 h. On the other hand, in the work of Li *et al.*[8] the introduction of a HCl washing and filtering step into the hydrothermal processing (which also used a 10–20% excess of Zn to be fed into the autoclave at the beginning) of $ZnGa_2O_4$ powders may originate from a need to leach out these GaO(OH) crystals, and we have hereby shown that the starting solutions do not need to be nonstoichiometric, in contrast to the work of Li *et al.*

Crystalline, single-phase $ZnGa_2O_4$ precipitates [with an experimental lattice parameter of 8.3350(2) Å] were recovered from the urea-rich solutions (i.e., U/C = 25.4, run 5) after 48 h of aging at 90 °C, followed by drying at 90 °C. The addition of 0.5 g of enzyme urease to the starting solutions was (in run 5 of Table I) able to produce single-phase $ZnGa_2O_4$ powders, only after 24 h of aging at 90 °C. Crystallinity of the powders, of run 5 or run 6, drastically increased with an increase in the post-synthesis calcination temperature, as shown by the XRD traces of Fig. 4. Formation of ceramics by enzyme-catalyzed reactions, which take place in aqueous solutions, has been successfully demonstrated and discussed by previous researchers.[18,19] Enzyme urease, when present in aqueous solutions together with urea, simply enhances the rate of decomposition of urea. Increasing the aging temperature from 90 to 120 °C, in run 7 of Table I, and decreasing the aging time from 48 to 24 h also produced single-phase zinc gallate powders, without using enzyme urease.

Figure 5 shows the FESEM micrographs of the same powders after calcination at different temperatures. Average particle (although being agglomerated) sizes measured directly from the FESEM micrographs were as follows; Fig. 5(a), 15 ± 3 nm, powders dried overnight at 90 °C; Fig. 5(b), 23 ± 3 nm, after calcination at 500 °C for 6 h; Fig. 5(c), 27 ± 3 nm, after calcination at 750 °C for 6 h; Fig. 5(d), 40 ± 5 nm, after calcination at 1000 °C for 6 h. The micrographs given in Figs. 5(e) and 5(f), on the other hand, were taken from the external surface of a pellet (prepared by cold-isostatic pressing, at 650 MPa, of powders precalcined at 750 °C for 6 h) heated at 1200 °C in air for 6 h. The results of chemical analyses for selected samples of this study are given in Table II. The lower Zn:Ga molar ratios (0.44) observed for the 1200 °C-heated samples indicated the evaporation of Zn at this temperature of calcination. $ZnGa_2O_4$ synthesized by the novel procedure described here were found to be stoichiometric.

The particle sizes reported by Hirano *et al.*[9] for the hydrothermally synthesized pure $ZaGa_2O_4$ powders [i.e., those which are not poisoned by the presence of GaO(OH) ellipsoids] were significantly larger

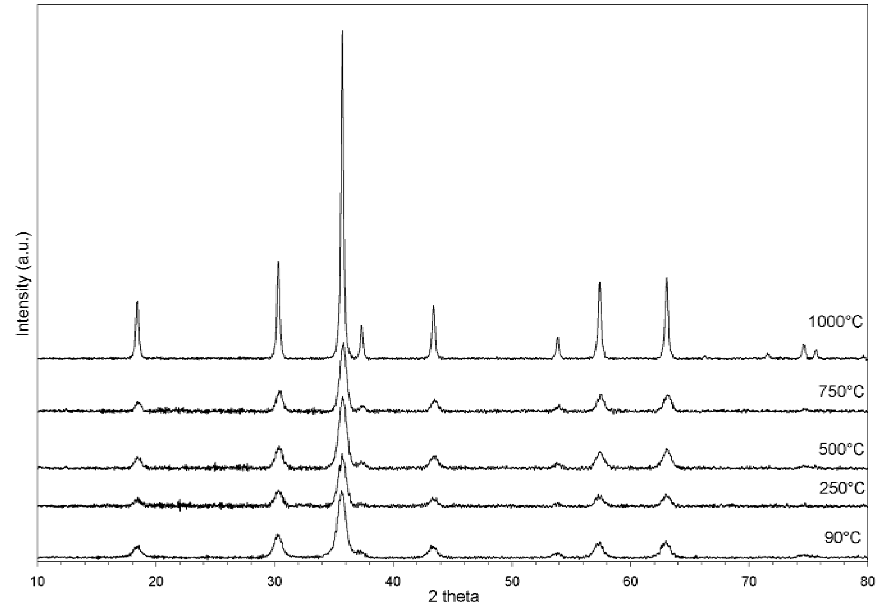

FIG. 4. XRD traces of precipitates obtained from run-5 solutions, as a function of calcination temperature in an air atmosphere.

(approximately 30–40 nm) than those of the current study, mainly because the autoclave temperature in their study needed to be raised to about 240 °C to form the single-phase spinel.

Results of the thermogravimetric/differential thermal analysis (TG/DTA) analyses are given in Fig. 6. The total weight loss (over the temperature range of 50 to 1080 °C), for the 90 °C-dried powders of run 5 of

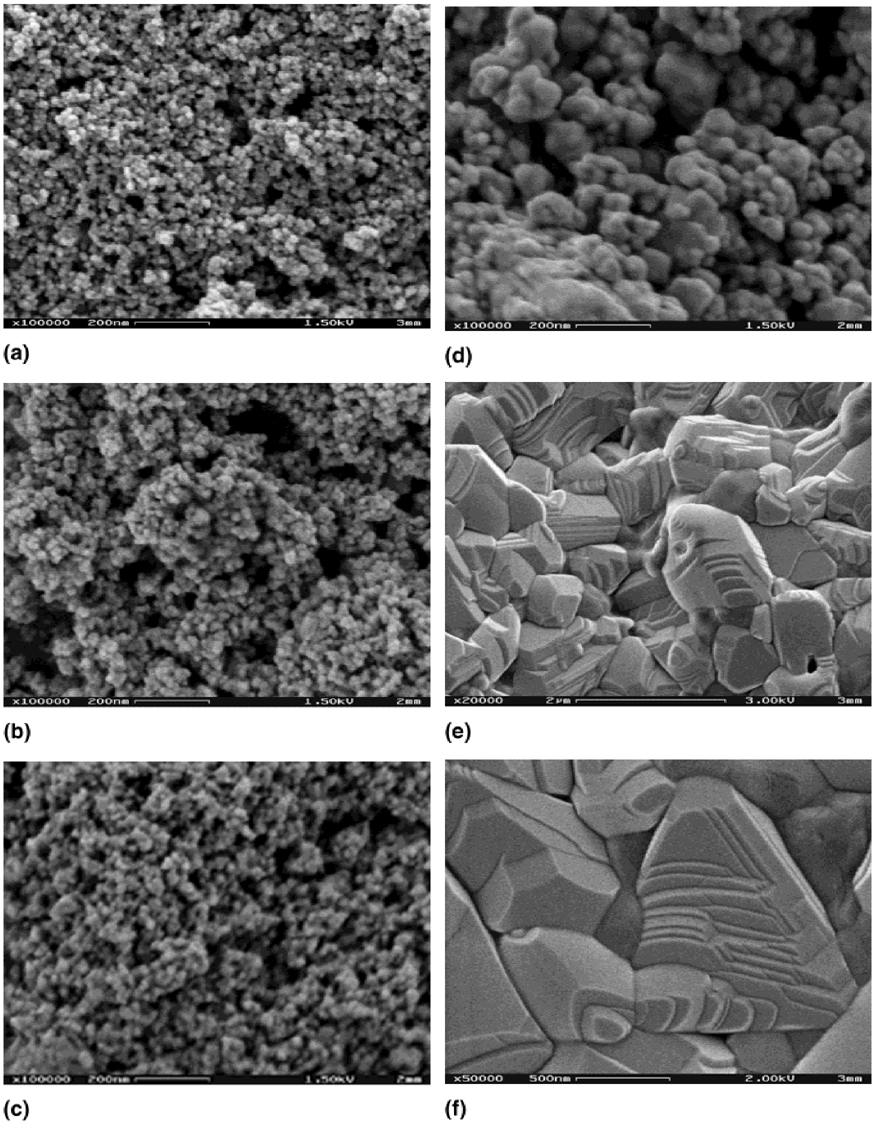

FIG. 5. SEM micrographs of run-5 powders, as a function of temperature: (a) 90 °C; (b) 500 °C; (c) 750 °C; (d) 1000 °C; (e,f) surface of a pellet of the same powders heated at 1200 °C.

TABLE II. Results of chemical analyses. (Nitrogen levels were below the detection limit for all samples.)

Sample	Zn/Ga (M)	Mn/Zn (M)	Mn/Ga (M)	Formula Nominal	Formula Measured	C (wt%)
Run 5 (90 °C)	0.5 ± 0.01	⋯	⋯	$ZnGa_2O_4$	$ZnGa_2O_4$	0.530
Run 5 (500 °C)	0.5 ± 0.01	⋯	⋯	$ZnGa_2O_4$	$ZnGa_2O_4$	0.280
Run 5 (750 °C)	0.5 ± 0.01	⋯	⋯	$ZnGa_2O_4$	$ZnGa_2O_4$	0.103
Run 5 (1000 °C)	0.5 ± 0.01	⋯	⋯	$ZnGa_2O_4$	$ZnGa_2O_4$	0.015
Run 5 (1200 °C)	0.44 ± 0.01	⋯	⋯	$ZnGa_2O_4$	$Zn_{0.87}Ga_2O_{3.87}$	0.012
Run 8 (90 °C)	0.497	0.006	0.003	$Zn_{0.994}Mn_{0.006}Ga_2O_4$	$Zn_{0.994}Mn_{0.006}Ga_2O_4$	0.520
Run 9 (90 °C)	0.450	0.111	0.050	$Zn_{0.9}Mn_{0.1}Ga_2O_4$	$Zn_{0.9}Mn_{0.1}Ga_2O_4$	0.530

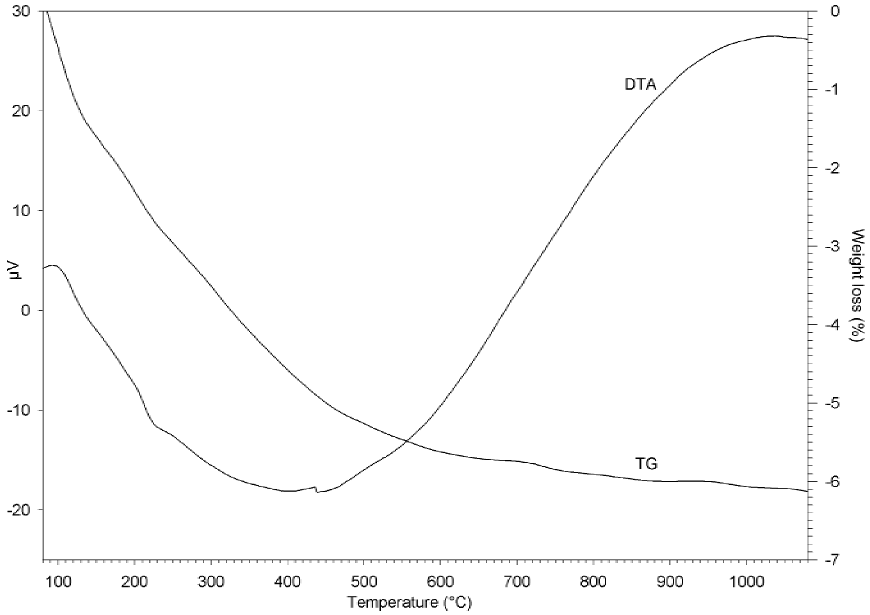

FIG. 6. TG/DTA plot of run-5 powders (air, 5 °C/min).

Table I, was found to be equal to 6.2%, and this figure corresponded to the gradual but smooth dewatering of the samples. The DTA curve, on the other hand, showed the continuous advance of a crystallization process, which take place over a significant range of temperatures extending beyond 440 °C.

FTIR spectra of crystalline $ZnGa_2O_4$ samples (run 5), as a function of calcination temperature, are given in Fig. 7. All of the IR spectra revealed the broad OH stretching band at around 3400 cm^{-1} and the H–O–H bending at 1630 cm^{-1}. The bands at 2344 and 1384 cm^{-1} were due to the adsorbed atmospheric CO_2. On the other hand, the group of weak bands at 1040 and 900 cm^{-1} were the constitutional M–OH bending bands. The bands, seen in samples calcined at ≤750 °C, in the interval of 1450–1405 cm^{-1} (including those in the range of 880 to 800 cm^{-1}) indicated the presence of structural CO_3^{2-} ions.[20] Nitrate ions were not detected in the samples, in accordance with the results of elemental N analyses. However, the presence of carbonate ions in the powders, which obviously resulted from the use of urea during aqueous synthesis, has also been confirmed by the elemental carbon analyses: samples dried at 90 °C had 0.530 ± 0.008% (by weight) C, whereas for the samples calcined at 1000 °C the same figure dropped to 0.015 ± 0.005%.

A. Mn-doped $ZnGa_2O_4$

The XRD patterns of the dried beige powders (of runs 8 and 9) are given in Fig. 8, as traces (b) and (c), respectively. Increasing the aging temperature of run 9 from 90 to 120 °C (in run 10 of Table 1) was observed to yield, again, Mn-doped $ZnGa_2O_4$ powders in 24 h. The filtered and dried (at 90 °C) powders of run 8 and run 9 both were found to be single-phase $ZnGa_2O_4$ spinel with the lattice parameter $a = 8.3349(2)$ Å. Inductively coupled plasma atomic emission spectroscopy analyses, Table II, showed the Mn to be incorporated at the desired level.

Chemical reactions relevant to the formation of $ZnFe_2O_4$ ceramics in ammonia-containing aqueous solutions via the hydrothermal method have recently been described by Yu *et al.*,[21] and the reactions given in that reference may also be used to explain the formation of $ZnGa_2O_4$ phosphor powders by the urea process presented here. As described above, α–GaOOH ellipsoids are the first crystalline phase to form in Zn, Ga, and urea-containing solutions, at a pH value of about 2. The precipitates recovered from all the liquors of Fig. 2 were found to be single-phase GaOOH. However, with prolonged aging (≥24 h) of these GaOOH ellipsoids in their mother liquor, they go through a dissolution/precipitation mechanism, as shown in Fig. 3(b).

As also shown above in the case of run 0, in which no Zn is present, following the initial precipitation of ellipsoidal particles of gallium oxide hydroxide, $Ga(OH)_4^-$ species are produced [according to the reaction $\alpha\text{–GaOOH} + 2H_2O = Ga(OH)_4^- + H^+$, which take place even in slightly basic solutions.][22] The existence and concentration of $Ga(OH)_4^-$ species in basic solutions are sustained by the solubility behavior of α–GaOOH as a function of pH.[22]

As stated by Yu *et al.*,[21] the metal ions Zn^{2+} may form different soluble Zn species, such as $ZnOH^+$, $HZnO_2^-$, ZnO_2^{2-}, and $Zn(NH_3)_n^{2+}$, due to the amphoteric property of Zn^{2+} and strong coordinating ability with NH_3. Soluble Zn species will react with $Ga(OH)_4^-$ to form spinel $ZnGa_2O_4$ by a homogeneous nucleation mechanism in bulk solution. Initial concentration of urea (and enzyme urease), the concentration of the decomposition products of urea, and the aging time are certainly the important factors that govern the formation of the spinel phase at 90 °C.

The presence of similar precipitation–dissolution–reprecipitation reactions has been previously observed and reported, for instance, by Ramanathan *et al.*[23] during the precipitation of crystalline boehmite [AlO(OH)] from solutions containing urea and Al nitrate, especially after prolonged aging of the mother liquors at 100 °C. Such dissolution–precipitation reactions, which usually needed significantly longer incubation times, were also observed

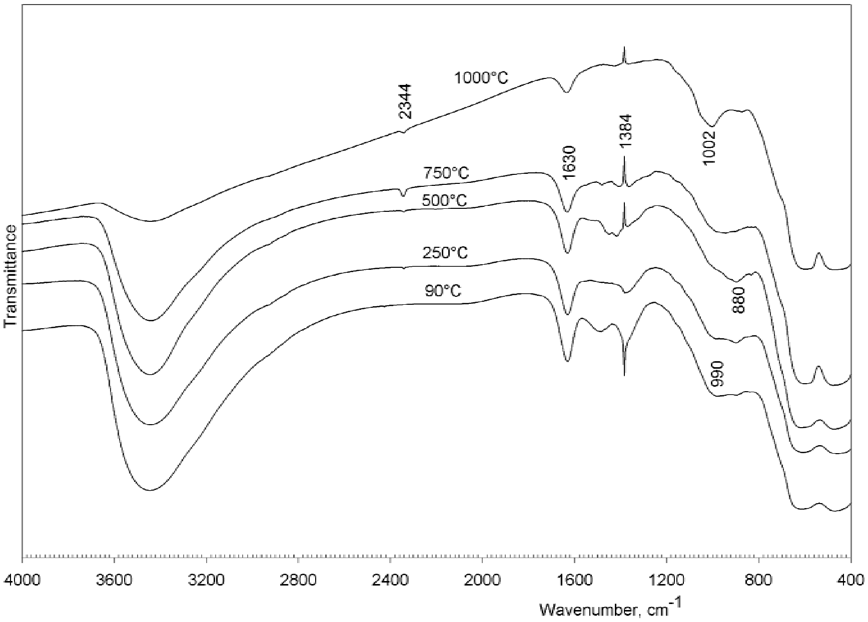

FIG. 7. FTIR spectra of run-5 powders, as a function of calcination temperature (1% KBr samples).

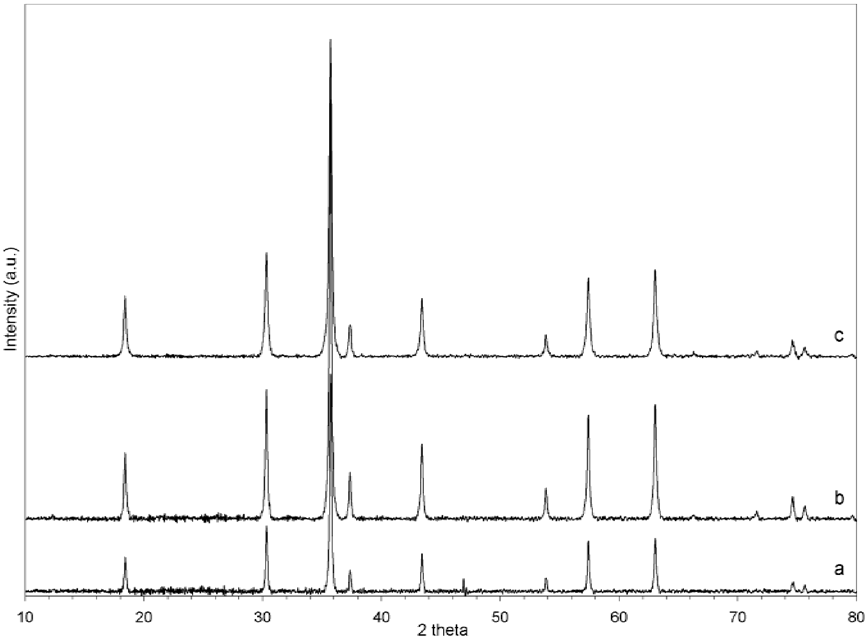

FIG. 8. XRD traces of pure and Mn-doped $ZnGa_2O_4$ samples calcined at 1000 °C: (a) run-5 sample, $ZnGa_2O_4$; (b) run-8 sample, $Zn_{0.994}Mn_{0.006}Ga_2O_4$; (c) run-9 sample, $Zn_{0.9}Mn_{0.1}Ga_2O_4$.

to take place in the hydrothermal synthesis of zeolites[24] and $BaTiO_3$[25,26] at <100 °C. Because of the poor coordinate bond forming ability of nitrate ions, they basically do not interfere with the ongoing reactions, and this explains why we did not observe (in elemental analyses) any N to be present in the formed precipitates. On the other hand, since the carbonate ions were one of the byproducts of urea decomposition, to a certain extent they were able to incorporate themselves into the formed precipitates, as evident from the data of Table II.

IV. CONCLUSIONS

Single-phase, crystalline, pure or Mn-doped $ZnGa_2O_4$ phosphor powders were synthesized *in situ* in urea-containing dilute (0.038 M) Zn and Ga nitrate solutions (urea-to-cation molar ratio ≈ 25) simply aged for 24–48 h in ordinary glass bottles in a laboratory oven at 90 °C, without any mixing or stirring. Urea concentration and aging time at 90 °C were critical parameters. There was no need to use a hydrothermal synthesis temperature >100 °C, and therefore, there was no need to use an autoclave to prepare the crystalline $ZnGa_2O_4$ spinel powders. Single-phase $ZnGa_2O_4$ powders filtered out from the bottles had an average particle size in the range of 15 to 18 nm. Even the powders filtered out from the mother liquors at lower aging times and lower urea concentrations were transformed into single-phase $ZnGa_2O_4$ upon calcination at ⩾900 °C. The same procedure was found to produce Mn-doped $ZnGa_2O_4$ powders as well. These powders may be suitable, e.g., for colloidal deposition-based thick film applications since they exhibit a total weight loss of only about 6.2% upon their heating to 1080 °C in air.

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