Preparation and characterization of bulk ZnGa$_2$O$_4$

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High-quality bulk ZnGa$_2$O$_4$ has been synthesized from equimolar mixtures of ZnO and Ga$_2$O$_3$ by the conventional solid-state method. For the first time, the sample has been characterized in detail to confirm the formation of pure single phase of spinel ZnGa$_2$O$_4$. The formation of ZnGa$_2$O$_4$ has been confirmed by sintering the mixtures of ZnO and Ga$_2$O$_3$ at different temperatures, ranging from 900–1200 °C. It is observed that the single phase of ZnGa$_2$O$_4$ has been formed at and above 1000 °C sintering temperature for 24 h. The crystallinity and phase formation of this single phase has been confirmed by X-ray diffraction. X-ray photoelectron spectroscopic studies have been carried out for bulk ZnGa$_2$O$_4$ sintered at 1000 °C for 24 h which showed 14% Zn, 28% Ga and 58% O, indicating stoichiometric ZnGa$_2$O$_4$. A new parameter, the energetic separation between the Zn 2p$_{3/2}$ and Ga 2p$_{3/2}$ peaks, has been used as a sensitive tool to distinguish between a complete formation of ZnGa$_2$O$_4$ compound and a mixture of ZnO and Ga$_2$O$_3$ powders. Surface morphology studies by scanning electron microscopy reveal that the formation of ZnGa$_2$O$_4$ takes place in mosaic rod-like structure. The purity of the compound has also been checked by the energy dispersive X-ray method, indicating the absence of foreign ions and the ratio of zinc to gallium has been calculated and found to be 1 : 2, indicating stoichiometric ZnGa$_2$O$_4$. © *1998 Kluwer Academic Publishers*

1. Introduction
A large class of compounds exhibits the spinel structure, the most interesting of which are the various magnetic insulators known as spinel ferrites. Attempts have been made by several investigators to prepare single-phase spinel structures like, ZnFe$_2$O$_4$, ZnAl$_2$O$_4$ ([1], and references therein) by the conventional solid-state route, as well as chemically precipitated mixtures. Recently, zinc gallate (ZnGa$_2$O$_4$) phosphors have gained much attention for use in vacuum fluorescent displays [2–4] and field emission display (FED) because they exhibit higher chemical stability than sulphide phosphors. FED has been of the most importance as a new kind of vacuum flat cathode ray tube. Among the techniques for the FED, high-purity low-voltage phosphor is one of the key issues needed to be solved. The ZnGa$_2$O$_4$ phosphor has been investigated for its good cathodoluminescence characteristics at low voltage [5]. The material ZnGa$_2$O$_4$ is a binary compound oxide consisting of ZnO and Ga$_2$O$_3$ which crystallizes in the spinel structure. It has an energy gap, E$_g$, of about 5.2 eV [6], and under excitation with ultraviolet light emits blue light due to transitions via a self activation centre. On the other hand, activation with Mn^{+2} ions shifts the emission to green [7]. The resulting emission band is attributed to the ^{4}T$_1$–^{6}A$_1$ inner atomic transition of the 3d electrons in the Mn^{+2} ion which is assumed, due to its same valence, to replace substitutionally the zinc atoms of the host material [8]. Another important application of the spinel structure is as one of the most interesting substrates for GaN deposition [9].

The aim of the present work was to prepare high-quality bulk ZnGa$_2$O$_4$ and deposit it on a suitable substrate, in order to study the deposition of GaN on ZnGa$_2$O$_4$ and also to make thin-film electroluminescent devices. Generally, it has been found that reaction sintering is difficult to control, especially when a chemically homogeneous, single-phase product with high purity, high density and uniform microstructure, is desired. In the present investigation, we have carried out the chemical reaction of equimolar mixtures of ZnO and Ga$_2$O$_3$ (commercial high-purity powders) prepared by the conventional solid-state route and for the first time it has been characterized by different techniques to illustrate the microstructural properties of bulk ZnGa$_2$O$_4$.

2. Experimental procedure
Ga$_2$O$_3$ powder, 10 g (reagent grade; purity 99.99%, Aldrich) was mixed with an equivalent molar quantity

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(4.3468 g) of ZnO powder (reagent grade; purity 99.99%, Aldrich) in an agate mortar and then 10 ml distilled ethylalcohol was added which was used as a dispersant to the above mixture. The slurry was mixed thoroughly for 3 h and then dried in oven at 100 °C for 24 h. The dried powder was ground lightly in an agate mortar and pestle and then passed through a 150 mesh sieve to eliminate any large agglomerates. Cylindrical compacts (10 mm diameter × 6 mm height) are prepared by die pressing at a pressure of 1 ton cm^{-2}. Sintering of the cylindrical compacts was carried out in air at constant heating rate of 3 °C min^{-1}, in the range 900–1200 °C for 24 h. The schematic flow chart of the synthesis of bulk ZnGa$_2$O$_4$ is shown in the Fig. 1. The sintered pellets have been ground in an agate mortar and pestle to fine powder and analysed by X-ray diffraction (XRD), energy dispersive X-ray analysis (EDX), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) techniques, to ascertain phase formation, elemental analysis, composition and morphology, respectively.

3. Results and discussion
3.1. Characterization of bulk ZnGa$_2$O$_4$
3.1.1. X-ray diffraction
X-ray diffraction (Siemens D5000) with copper target, K_α radiation ($\lambda = 0.15406$ nm) is used for phase identification. Fig. 2 shows the XRD pattern of the ZnO and Ga$_2$O$_3$ powder mixtures sintered at 900 °C for 24 h. This spectrum clearly shows that the formation of ZnGa$_2$O$_4$ is not completed at a sintering temperature
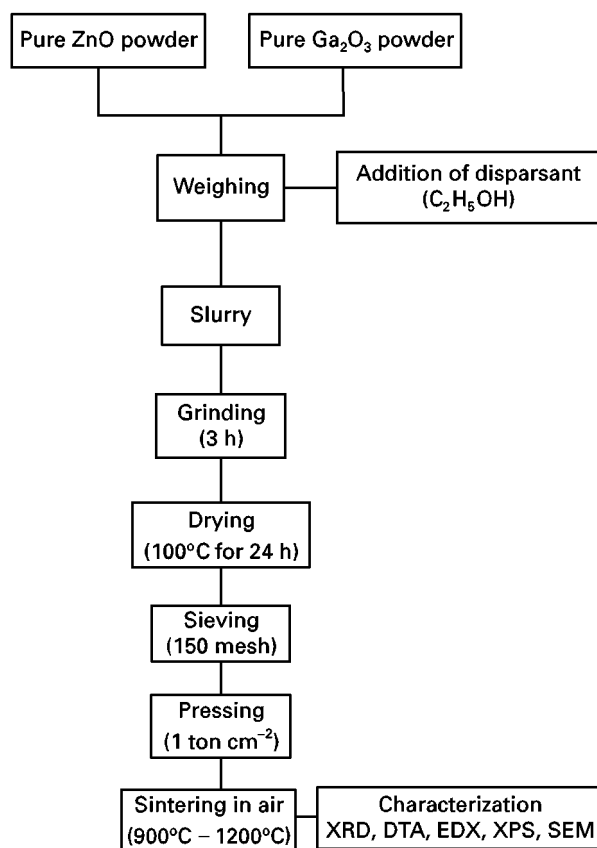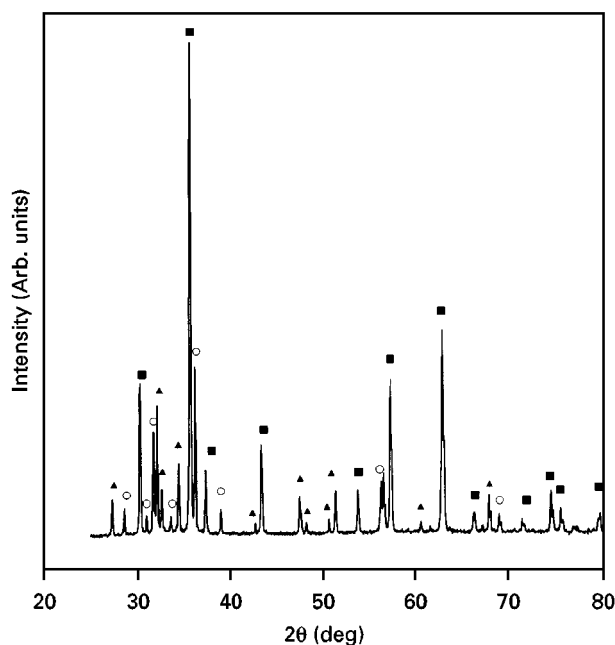

Figure 2 X-ray diffraction pattern of ZnGa$_2$O$_4$ sintered at 900 °C. (■) ZnGa$_2$O$_4$, (○) ZnO, (▲) Ga$_2$O$_3$.
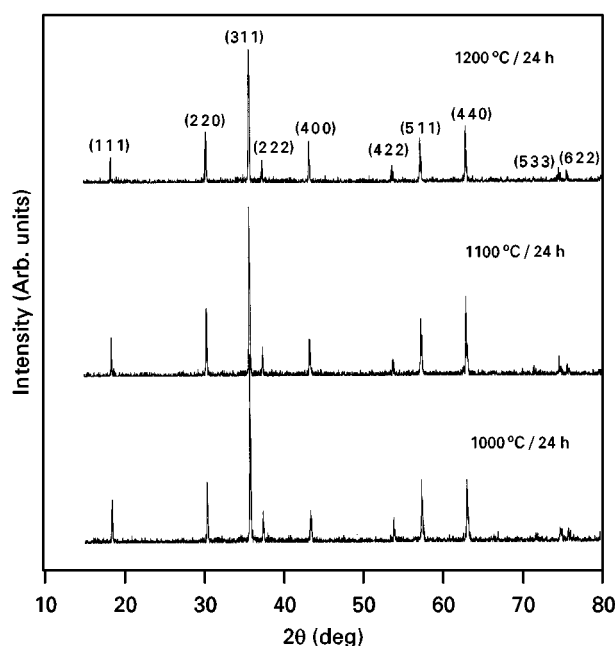

Figure 3 X-ray diffraction pattern of pure bulk ZnGa$_2$O$_4$ sintered at different temperatures.

of 900 °C, showing the mixtures of unreacted ZnO and Ga$_2$O$_3$. Fig. 3 shows the formation of single phase ZnGa$_2$O$_4$ at a sintering temperature of 1000 °C for 24 h. The effects of sintering temperature on crystallographic structure and crystallite size for the sample sintered at 900 °C revealed low intensity and broad peaks, indicating the crystallinity is not well defined. In order to obtain higher resolution, measurements were performed keeping the monochromator in parallel, to increase the X-ray path lengths in the samples as well as to obtain improved full-width at half-maximum (FWHM) and intensity. Sharp and intense

Figure 1 Schematic flow chart of the synthesis of bulk ZnGa$_2$O$_4$.

peaks are observed for the samples sintered at and above 1000 °C, indicating a higher degree of crystallinity. All the diffraction lines agree with reported values and match the cubic structure of JCPDS data (card 38-1240) confirming the formation of $ZnGa_2O_4$. From the spectra, the lattice parameters have been calculated and found to be $a = 0.83313$ nm which is in good agreement with the reported value ($a = 0.83349$ nm) from the JCPDS data. The samples sintered at 1100 and 1200 °C for 24 h are also presented, showing the stability of the $ZnGa_2O_4$ compound even at higher temperatures. The average crystallite size is calculated and found to be 58 nm by the Scherrer formula applied to the (3 1 1) orientation which is the maximum reflection of the cubic structure of $ZnGa_2O_4$ at $2\theta = 35.8°$.

3.1.2. Thermogravimetric and differential thermal analysis

Thermogravimetric analysis as well as differential thermal analysis of the sample sintered at 1000 °C for 24 h have been carried out to determine the weight loss as well as the exact temperature for the formation of $ZnGa_2O_4$. The differential thermal analysis (DTA) and thermogravimetric analysis (TGA) curves for $ZnGa_2O_4$ powder in the temperature range 20–1200 °C at a heating rate of 10 °C min^{-1} are shown in the Fig. 4. The TGA curve indicates that there is a negligible weight loss between 405 and 410 °C. On the other hand, we have observed an endothermic peak at 995 °C, which is due to the heat lost during the formation of single-phase $ZnGa_2O_4$ from the mixtures of ZnO and Ga_2O_3. This has been further confirmed by the X-ray diffraction technique for the same sample sintered at 1000 °C for 24 h by which we have observed the formation of single-phase $ZnGa_2O_4$.

3.1.3. Energy dispersive X-ray analysis

Energy dispersive X-ray analysis has been carried out to determine the elemental analysis of the prepared bulk $ZnGa_2O_4$. Fig. 5 shows the EDX spectrum of bulk $ZnGa_2O_4$ sintered at 1000 °C for 24 h showing the presence of elemental zinc, gallium and oxygen in
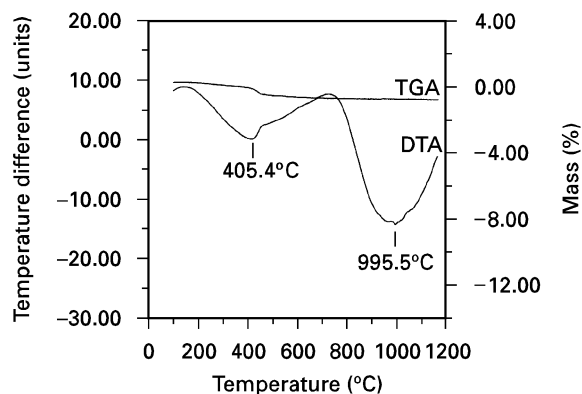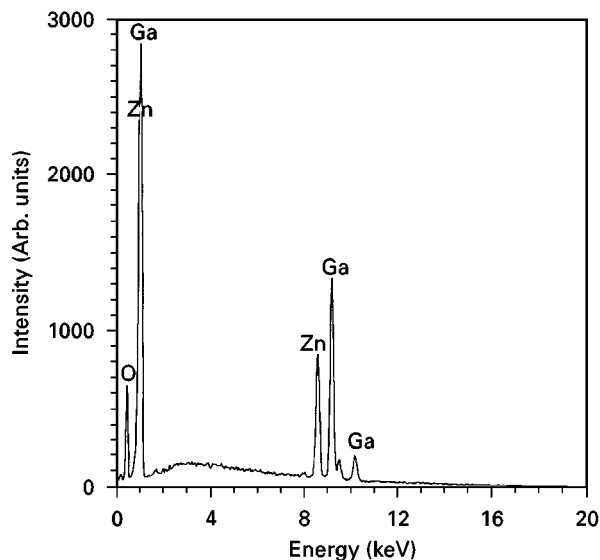

Figure 5 Energy dispersive X-ray analysis of pure $ZnGa_2O_4$ sintered at 1000 °C.

the bulk and indicating the purity of the compound. The atomic concentrations of zinc and gallium have been calculated and found to be 32% and 68%, respectively, when compared to 33% Zn and 67% Ga in stoichiometric $ZnGa_2O_4$. The same behaviour has been observed for the samples sintered at 1100 and 1200 °C. The sample sintered at 1000 °C for 24 h was also tested by X-ray fluorescence analysis (which is not shown), where we have obtained ZnO to be 52.7 wt % and that of Ga_2O_3 to be 47.3 wt % with 0.05% carbon.

3.1.4. Scanning electron microscopy

Fig. 6 shows scanning electron micrographs of bulk $ZnGa_2O_4$ samples after sintering at 900, 1000, 1100 and 1200 °C, respectively. The sample sintered at 900 °C shows flake-like structures of $ZnGa_2O_4$ and fine particles of unreacted ZnO as well as Ga_2O_3. On the other hand, samples sintered at and above 1000 °C for 24 h show uniform mosaic rod-like structures of $ZnGa_2O_4$ surrounded by fine particles of $ZnGa_2O_4$.

3.1.5. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopic studies of the samples sintered at 900, 1000 and 1100 °C for 24 h have been performed using the PHI ESCA system equipped with an Al K_α photon source ($hv = 1486.6$ eV) and a concentric hemispherical analyser. Fig. 7 shows the survey scan acquired in the range 0–1200 eV of the powders of Ga_2O_3 and ZnO and of the $ZnGa_2O_4$ sample sintered at different temperatures. No contaminant species are detectable within the sensitivity of the technique. Only a very low peak from adsorbed carbon is present on the spectra. In Fig. 8 the detailed spectra of the Ga 2p and Zn 2p peaks from the different samples are shown. The binding energy (BE) calibration of the spectra has been referred to carbon 1s peak, located at BE = 285.0 eV [10]. From the
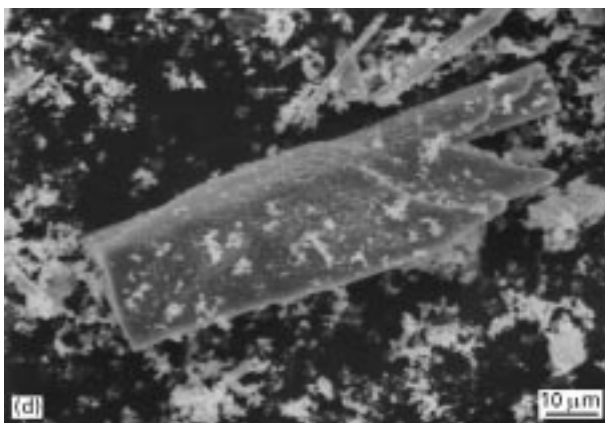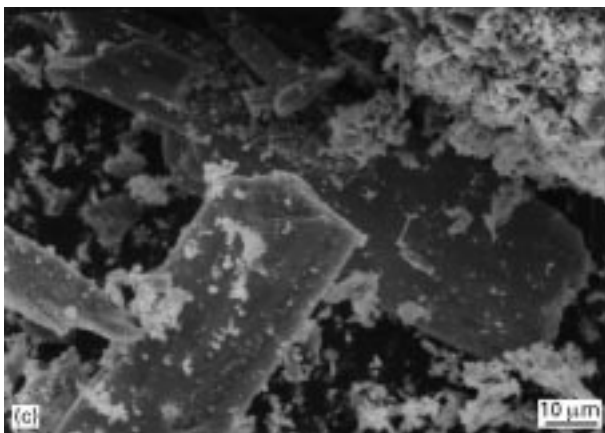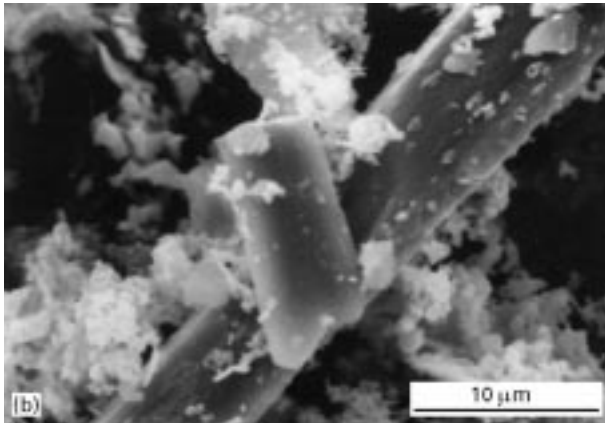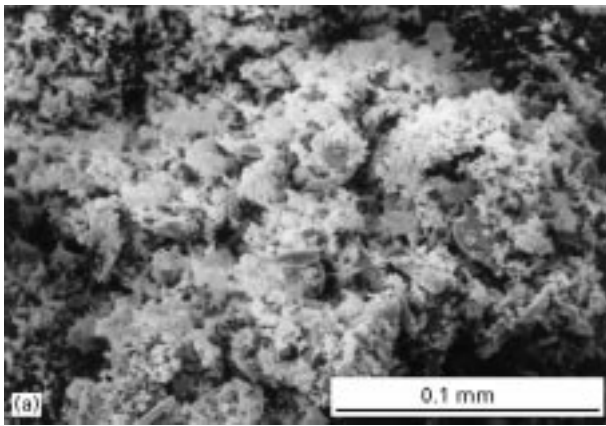

Figure 4 Thermogravimetric and differential thermal analysis of pure bulk $ZnGa_2O_4$.

Figure 6 Scanning electron micrographs of pure $ZnGa_2O_4$ sintered at different temperatures: (a) 900 °C, (b) 1000 °C, (c) 1100 °C (d) 1200 °C.
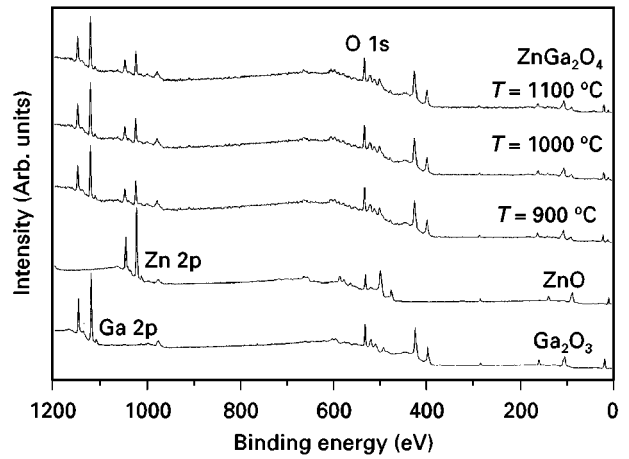

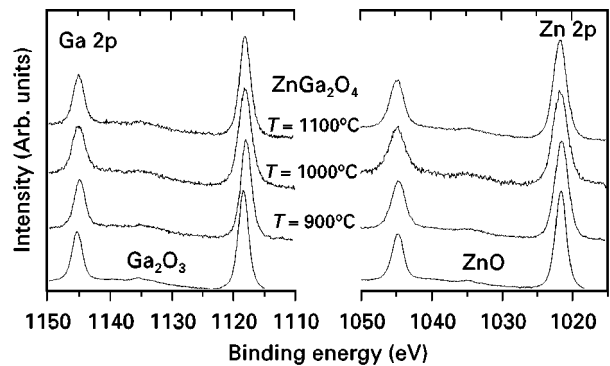Figure 7 X-ray photoelectron spectroscopy survey scan of bulk Ga_2O_3, ZnO and $ZnGa_2O_4$ taken at different temperatures.

Figure 8 Detailed XPS spectra of Ga 2p and Zn 2p of bulk Ga_2O_3, ZnO and $ZnGa_2O_4$ taken at different temperatures.

detailed spectra of the Zn 2p, Ga 2p and O 1s peaks of the sintered samples, by using the tabulated sensitivity factors (3.72 for gallium, 3.73 for zinc and 0.71 for oxygen) [10], we found 1:2 for zinc and gallium and 1:4 for zinc and oxygen, indicating the stoichiometric composition of $ZnGa_2O_4$ for all the sintered samples. This result is in contrast to the X-ray diffraction analysis, where we have obtained the correct crystalline structure of $ZnGa_2O_4$ for the samples sintered at and above 1000 °C.

One parameter independent of the energy calibration is the separation between the $Zn\,2p_{3/2}$ and $Ga\,2p_{3/2}$ peaks, which is reported in Table I. From the table, we can observe that, as the sintering temperature decreases, this separation increases from $\Delta E = 96.3\,eV$ (for the highest temperature) to $\Delta E = 96.7\,eV$ obtained from the independent precursors powders of ZnO and Ga_2O_3. This suggests an incomplete formation of the $ZnGa_2O_4$ compound and it is in agreement with the results obtained in the X-ray diffraction analysis. In fact, for the sample sintered at 900 °C for 24 h, a mixture of ZnO, Ga_2O_3 and $ZnGa_2O_4$ was found by means of XRD measurements. Furthermore, these results show that the XPS compositional analysis, obtained from peak area values, is not always able to distinguish between

TABLE I Separation between the Zn $2p_{3/2}$ and Ga $2p_{3/2}$ peaks

Temperature (°C)	Ga $(2p_{3/2})$–Zn $(2p_{3/2})$ (energy separation) (eV)
Independent powders	96.7
900	96.5
1000	96.3
1100	96.3

a mixture of ZnO, Ga_2O_3 and a stoichiometric $ZnGa_2O_4$ sample. In fact, an equimolar mixture of ZnO, Ga_2O_3 and $ZnGa_2O_4$ compound has the same atomic percentage concentration. Instead, the energetic separation between the Zn $2p_{3/2}$ and Ga $2p_{3/2}$ peaks, may be a useful parameter for a more careful characterization of these samples.

4. Conlusions

We have synthesized high-purity bulk single-phase $ZnGa_2O_4$ from equimolar mixtures of ZnO and Ga_2O_3. The formation of this single phase has been confirmed by X-ray diffraction for the samples sintered at and above 1000 °C for 24 h. The purity of the compound has been confirmed by energy dispersive X-ray analysis as well as X-ray photoelectron spectroscopy studies indicating the absence of foreign ions and the exact percentages of composition, 14% Zn, 28% Ga and 58% O in bulk $ZnGa_2O_4$. Scanning electron microscopic studies of $ZnGa_2O_4$ powders sintered at and above 1000 °C for 24 h reveals the mosaic rod-like structure. A new parameter, i.e. the energetic separation between the Zn $2p_{3/2}$ and Ga $2p_{3/2}$ peaks, has been introduced as a sensitive tool to distinguish between a complete formation of the $ZnGa_2O_4$ compound and a mixture of ZnO and Ga_2O_3 powders.

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