

# New combustion synthesis technique for the production of $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ powders: Hydrazine/metal nitrate method

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A new low-temperature method to produce  $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$  ( $x = 0.1, 0.2$ , and  $0.3$ ) powders with high purity, high chemical homogeneity and improved crystallinity in the as-synthesized state has been developed. This procedure produced finely divided powders through an exothermic reaction between the precursors. The process starts with aqueous solutions of  $\text{In}(\text{NO}_3)_3$  and  $\text{Ga}(\text{NO}_3)_3$  as the precursors and hydrazine as the (noncarbonaceous) fuel. The combustion reaction occurred when heating the precursors between  $150$  and  $200^\circ\text{C}$  in a closed vessel filled with an inert gas (Ar), which yields  $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$  directly. These materials were compared with powders prepared by a more typical combustion synthesis reaction between nitrates and a carbonaceous fuel at a higher ignition temperature of  $500^\circ\text{C}$ .

## I. INTRODUCTION

Complex oxide compositions have increasing importance for various applications such as ferroelectrics for dynamics random access memories ( $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ ), high- $T_c$  superconductors ( $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ), and luminescent materials for information display applications [ $(\text{Y}_{1-x}\text{Tb}_x)\text{Al}_5\text{O}_{12}$ ]. Indium gallium oxide powder [ $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$ ] is used in spectroscopic analysis and, as an evaporated film, provides protective coating for metal mirrors, as sputtering target for transparent conductive films for electro-optical displays. In addition, it can be used as a precursor to produce indium gallium nitride powders ( $\text{In}_x\text{Ga}_{1-x}\text{N}$ ), a luminescent and promising material for optoelectronic devices, low-cost solar cells with high efficiency, optical coatings, and various types of sensors.<sup>1,2</sup>

The synthesis of fine and uniform crystallite size, chemical homogeneous, high-purity, complex oxide formulations has been the study for the past few decades. At present, there are many techniques to synthesize complex oxides such as sol-gel processing, precipitation from aqueous solutions, hydrothermal synthesis and combustion synthesis.<sup>3</sup>

Combustion synthesis is an important processing method that produces nanocrystalline, high-purity, single-phase complex oxide powders in the as-synthesized state.<sup>4-6</sup> Combustion synthesis is a self-sustaining, self-propagating technique that is based on an anionic oxidation-reduction reaction.<sup>7</sup> A highly

exothermic reaction occurs between metal nitrates and a carbonaceous reductive fuel, resulting in a porous, voluminous material due to the high quantity of escaping gases produced during the reaction.<sup>8</sup> Combustion synthesis is typically conducted with a carbonaceous reductive fuel (e.g., carbonylhydrazide,  $\text{CH}_6\text{N}_4\text{O}$ ) and metal nitrates that are dissolved in water and placed into a muffle furnace preheated to approximately  $500^\circ\text{C}$  open to the atmosphere.<sup>9</sup> Often, undesirable impurities such as carbon and nitrogen, are commonly found in the product.

The mechanism for combustion synthesis has been studied during the last decade. It was found that the combustion process is controlled by the heating rate, the fuel to oxidizer ratio, type of fuel, ignition temperature and volume of precursors. Kingsley and Patil<sup>10</sup> reported that fuel-rich combustion mixtures yielded products with carbon impurity and that the precursor mass/reaction vessel volume ratio is critical for the exothermic gas phase reaction to occur. Another study by Zhang and Stangle<sup>8</sup> indicated that the reaction temperature and the reaction time are two important factors that control the phase development during the process. The optimal temperature/time conditions vary from material to material and are determined primarily by the intrinsic phase transformation temperature that is characteristic of each system. Ekambaram and Patil<sup>11</sup> synthesized yttrium oxide by the combustion processes, and it was found that the surface area of yttria depended on the type of fuel used. This was attributed to the different exothermic energies of the fuels.

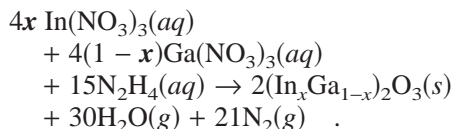
In this work, a new method of producing complex oxide powders with a higher purity, higher crystallinity, larger particle size than powders obtained from the usual combustion synthesis techniques is reported. Combustion synthesis using hydrazine ( $\text{N}_2\text{H}_4$ ) with metal nitrates was conducted in a controlled environment at low temperatures (approximately  $200^\circ\text{C}$ ).

Hydrazine is a strong reducing agent that is used in processes of corrosion protection and pollution control.<sup>12</sup> However, in the gas phase, it forms explosive mixtures with air when its concentration is  $>4.7\%$  by volume. For safety reasons, the aqueous form is generally sold commercially,<sup>13</sup> the most common composition being hydrazine monohydrate ( $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ ). Hydrazine can be used for power generation in propulsion applications such as thrusters for orbiting satellites. Hence, hydrazine handling must be taken carefully into inert environments, and the reactions with the oxide precursors should be performed in a high-pressure reaction vessel.

The goal was to prepare an intimate mixture of a reducing agent (hydrazine) and an oxidizing agent (metal nitrates) in conjunction with the requisite ratio of indium and gallium. The mixture should ignite at low temperature and be capable of a self-sustained, fast reaction to form the oxide product. In addition, it was desired to compare identical reaction product compositions between the hydrazine/metal nitrates and the more studied carbonaceous fuel/metal nitrates methods.

## II. EXPERIMENTAL PROCEDURE

The procedure for the combustion synthesis of  $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$  for  $0 \leq x \leq 1$  is illustrated in Fig. 1. The precursors were  $\text{In}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ ,  $\text{Ga}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , and  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ . The required mass of each reactant was calculated from the desired mass of the products, according to the following chemical equation:



The nitrates were then allowed to dissolve into the beaker. The beaker was then introduced into a glove box with an argon atmosphere. A 1.5-ml of 98.5% hydrazine was added and a viscous solution was formed. Then the beaker was removed from the glove box and quickly introduced into the reactor, which was then tightly closed.

The advantages of using a reactor to conduct the combustion synthesis reactions on the open furnace are as follows: (i) personal safety due to the properties of fuel (hydrazine); (ii) total recuperation of produced material, which because of violent reaction goes away from the

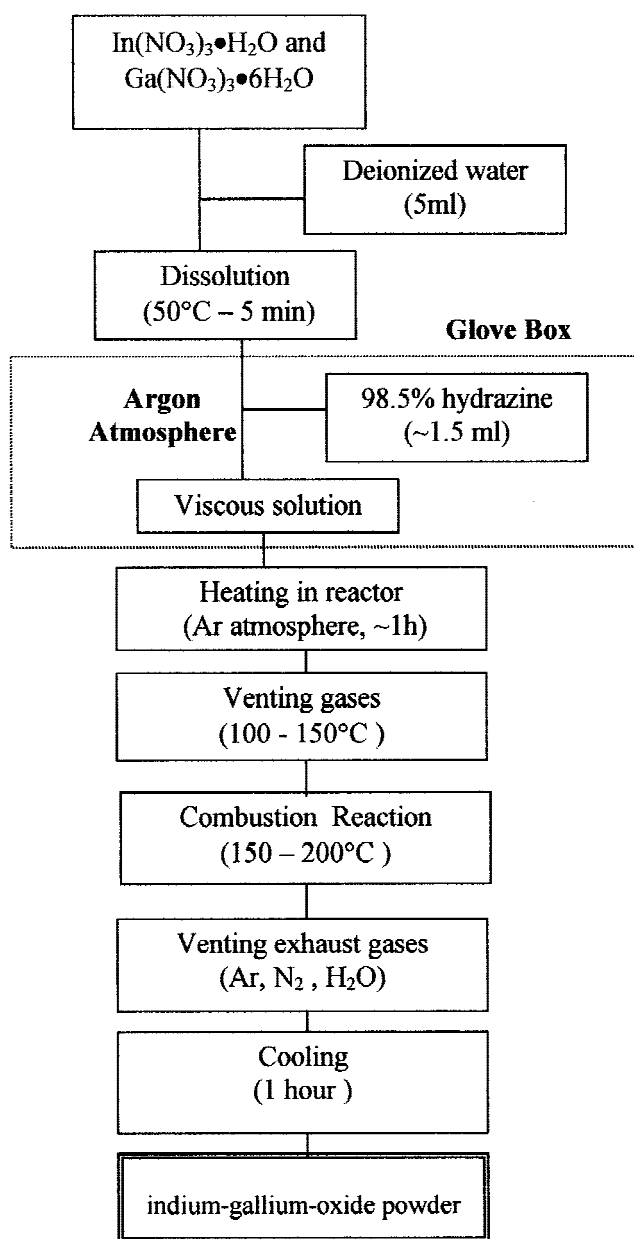


FIG. 1. Flow diagram of the combustion synthesis process of  $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$  using hydrazine fuel.

beaker; (iii) precise control of parameters of reaction, is possible to measure temperatures, pressures, and flows; and (iv) atmosphere controlled, reactive or inert according to reaction.

A schematic representation of combustion synthesis reactor is shown in Fig. 2. The reaction vessel, part of the reactor, is equipped with a gas inlet valve for charging gas into the reactor; a gas release valve for withdrawing gas or releasing pressure; a dip tube connected to the inlet valve; a pressure gauge; a safety rupture disk; a thermocouple for temperature measurements; and electric heating and automatic temperature control.

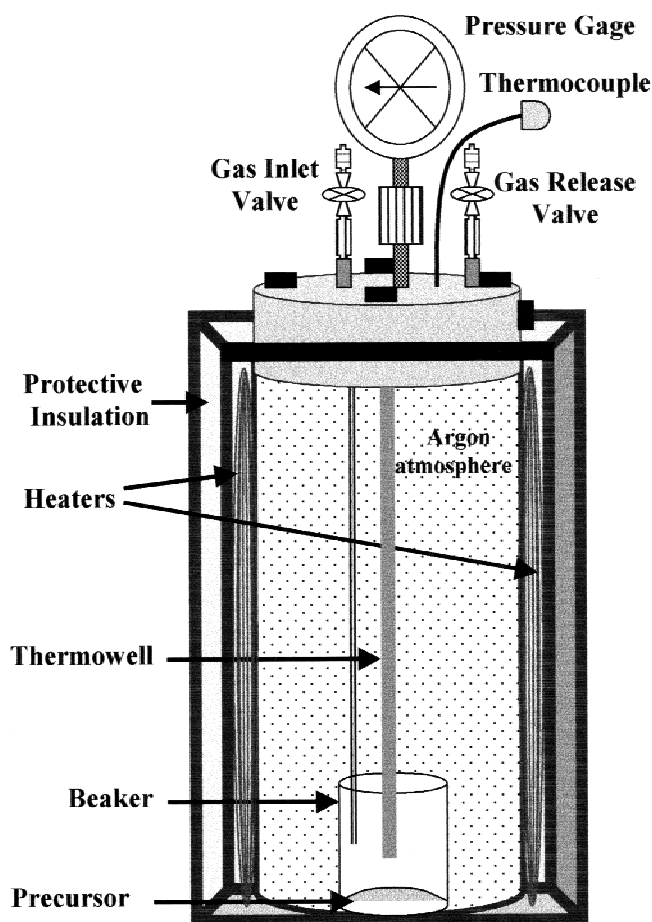
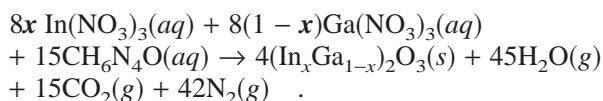


FIG. 2. Schematic representation of combustion synthesis reactor.

Once the reactor has been closed, an argon flow (200 ml/min) was supplied through the inlet valve to remove the air from the reactor and to form an inert atmosphere. The argon continually flowed through and released the reactor to the atmosphere via the gas release valve, thereby the reaction was conducted at a pressure of 1 atmosphere. The heater was turned on, and the ignition temperature of the reaction occurred between 150 and 200 °C as measured with the thermocouple. Once the reaction had gone to completion, the beaker was removed from the reaction vessel and allowed to cool down to room temperature. By using the more traditional combustion synthesis method, metal nitrates  $[\text{In}(\text{NO}_3)_3$  and  $\text{Ga}(\text{NO}_3)_3]$  and a carbonaceous fuel (carbohydrazide,  $\text{CH}_6\text{N}_4\text{O}$ ) were reacted to produce  $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$  for  $0 \leq x \leq 1$  powders, for comparison purposes. The method is described with more detail in Ref. 9. In this case the reaction shown below was ignited in air at 500 °C,



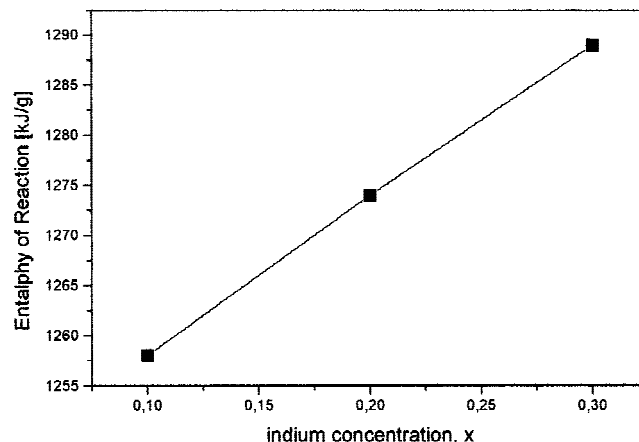
Powder x-ray diffraction data were obtained by using a  $\theta$ - $2\theta$  diffractometer excited with  $\text{CuK}\alpha$  ( $\lambda = 0.15406$  nm) radiation. The crystallite size of the powders was calculated from the angular width of the most intense peak [002] by comparison to a polysilicon standard using the Scherrer formula.<sup>14</sup> The morphology of the powders was studied with a scanning electron microscope (SEM) operated at 10 kV. The elemental composition of the powders was determined by means of x-ray photoelectron spectroscopy (XPS) using an Al anode with a characteristic x-ray energy of 1486.6 eV. The base pressure was approximately  $2 \times 10^{-9}$  torr. Cleaning of the surface before measurements was done with  $\text{Ar}^+$  sputtering during 5 min with a beam energy of 4 keV and a beam current of  $0.36 \mu\text{A}/\text{cm}^2$ . The composition of the  $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$  powders was determined by energy-dispersive x-ray (EDX) analysis. An acceleration voltage of 10 kV was used.

### III. RESULTS AND DISCUSSION

$(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$  with  $x = 0.1, 0.2$ , and  $0.3$  were fabricated with the new method (hydrazine/metal nitrate, HMN) and the more traditional method (carbohydrazide/metal nitrate, CMN).

For the HMN method, precursors mixture contained fuel reacted strongly in contact with the hot vessel, releasing gases and heat. The reaction, once ignited, was found to propagate in a self-sustaining manner. Several small fragments were found on the wall of the reaction vessel, emitted from the combustion mixture because of the vigorous nature of the reaction.

The determined enthalpies of reaction ( $\Delta H_R$ ) varies linearly with respect to indium concentration (see Fig. 3) from  $-10.016$  kJ to  $-9.540$  kJ per gram of oxide produced as shown in Table I. The enthalpies of each reactant and product at different temperatures were consulted in the thermodynamic tables.<sup>15-17</sup>

FIG. 3. Enthalpies of reaction at 298.15 K—indium concentration ( $x$ ) for  $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$  powders synthesized by the hydrazine/metal nitrate method.

Considering an adiabatic process at constant pressure (atmospheric), the enthalpy of the system is constant; therefore, the sum of the enthalpies of the products is the same as the sum of the enthalpies of the reactants. The final temperature (adiabatic temperature,  $T_{\text{ad}}$ ) of the reaction can be determined by plotting the enthalpies of reactants and products over the temperature range. Linear interpolation between the sums of the enthalpies of the products at 800 K and 1600 K reveals that  $T_{\text{ab}} = 1258$  K to  $x = 0.1$ ,  $T_{\text{ab}} = 1274$  K to  $x = 0.2$ , and  $T_{\text{ab}} = 1289$  to  $x = 0.3$ . The enthalpies of reactants and products at different temperatures were consulted in the thermodynamic tables.<sup>15–17</sup> As we can see in Fig. 4, as enthalpy of reaction ( $\Delta H_R$ ), also the final temperature in the reaction vessel varies linearly with respect to indium concentration.

X-ray diffraction results show that the oxides produced with the HMN technique have a better crystallinity compared with the powders produced with the CMN. The HMN reactions produce sharper and narrower peaks compared with the CMN reaction, as shown in Figs. 5(a) and 5(b). Both show a decrease in crystallite size as the concentration of indium  $x$  increased; however, the crystallite size of powders from the HMN reaction is from two to seven times larger than in powders from the CMN reaction (see Table II). The x-ray diffraction spectra of the  $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$  powders produced by both techniques

TABLE I. Enthalpies of reaction at 298.15 K and final temperatures at different indium concentrations ( $x$ ) for  $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$  powders synthesized by the hydrazine/metal nitrate method.

Compound	Enthalpy of reaction $\Delta H_R$ (kJ/g)	Final temperature (K)
$(\text{In}_{0.1}\text{Ga}_{0.9})_2\text{O}_3$	-10.016	1257.7
$(\text{In}_{0.2}\text{Ga}_{0.8})_2\text{O}_3$	-9.768	1273.64
$(\text{In}_{0.3}\text{Ga}_{0.7})_2\text{O}_3$	-9.540	1289.20

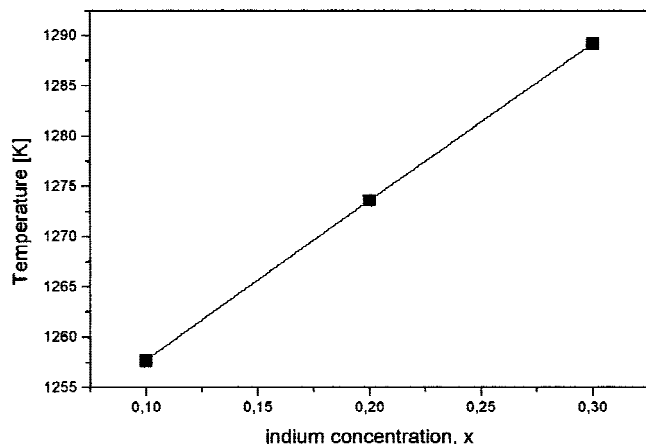


FIG. 4. Final temperature—indium concentration ( $x$ ) for  $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$  powders synthesized by the hydrazine/metal nitrate method.

[Figs. 5(a) and 5(b)] show a shift of the main peaks toward the left, because of the increase of the concentration of indium into the monoclinic structure of gallium oxide.

SEM images of the  $(\text{In}_{0.1}\text{Ga}_{0.9})_2\text{O}_3$  powders produced by both methods are shown in Figs. 6(a) and 6(b). The particle-size distribution of the powders synthesized by the HMN reaction is narrow, between 3 and 6  $\mu\text{m}$ . The

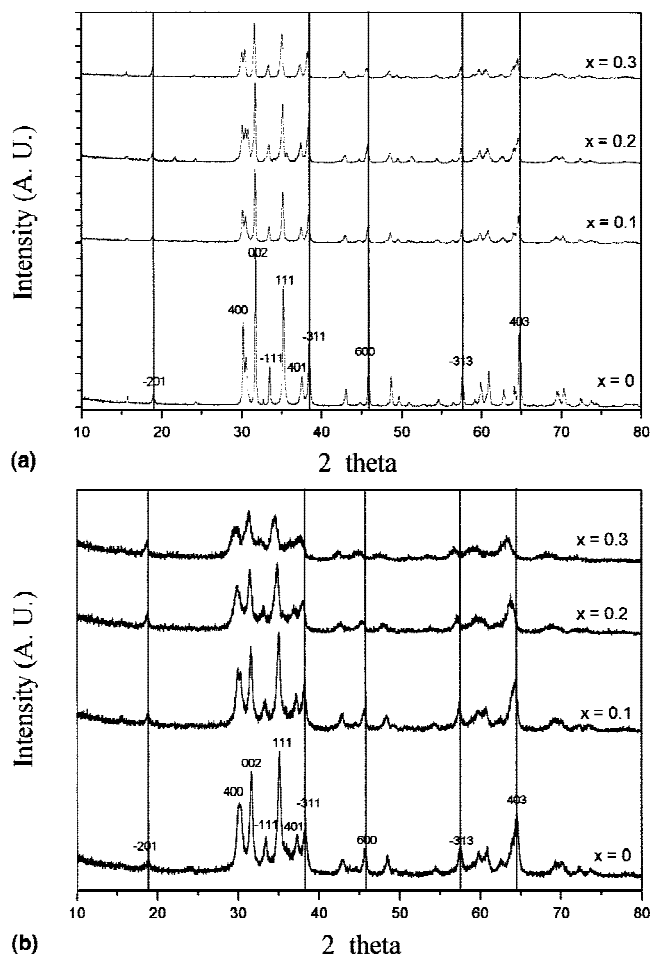


FIG. 5. (a) X-ray diffraction spectra for powders  $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$  produced by combustion synthesis of a hydrazine/metal nitrate mixture. (b) X-ray diffraction spectra for powders  $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$  produced by combustion synthesis of a carbohydrazide/metal nitrate mixture.

TABLE II. The crystallite size for  $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$  powders estimated by XRD.

Compound	Hydrazine/metal nitrate method (nm)	Carbohydrazide/metal nitrate method (nm)
$\text{Ga}_2\text{O}_3$	>200	31
$(\text{In}_{0.1}\text{Ga}_{0.9})_2\text{O}_3$	159	26
$(\text{In}_{0.2}\text{Ga}_{0.8})_2\text{O}_3$	83	40
$(\text{In}_{0.3}\text{Ga}_{0.7})_2\text{O}_3$	54	26

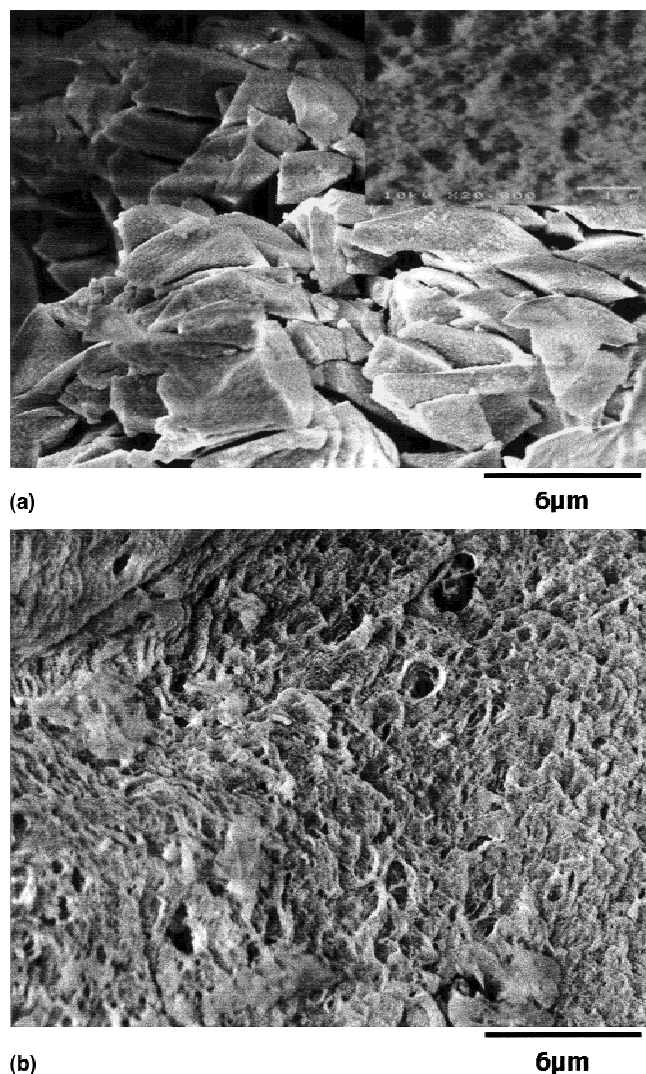


FIG. 6. (a) Scanning electron micrograph of  $(\text{In}_{0.1}\text{Ga}_{0.9})_2\text{O}_3$  powders produced by combustion synthesis of a hydrazine/metal nitrate mixture. (b) Scanning electron micrograph of  $(\text{In}_{0.1}\text{Ga}_{0.9})_2\text{O}_3$  powders produced by combustion synthesis of a carbohydrazide/metal nitrate mixture.

morphology of the powders is a mixture of high porous particles with plakelike shape. The powders synthesized by CMN method show a foamy microstructure with no measurable particles-size present. To obtain particles by the CMN method, it is necessary to grind the reaction product. Hand grinding in a mortar and pestle for a few minutes typically results in particles approximately  $11.2\text{ }\mu\text{m}$  in size.<sup>14</sup>

XPS results of the  $(\text{In}_{0.1}\text{Ga}_{0.9})_2\text{O}_3$  powders synthesized by both methods are shown in Figs. 7(a) and 7(b). The main XPS transitions of indium–gallium–oxide are shown in Fig. 7(a) for the powder synthesized by HMN reaction, and there is no appreciable contamination of other elements. Figure 7(b) shows the main XPS transitions of indium–gallium–oxide for the powders produced

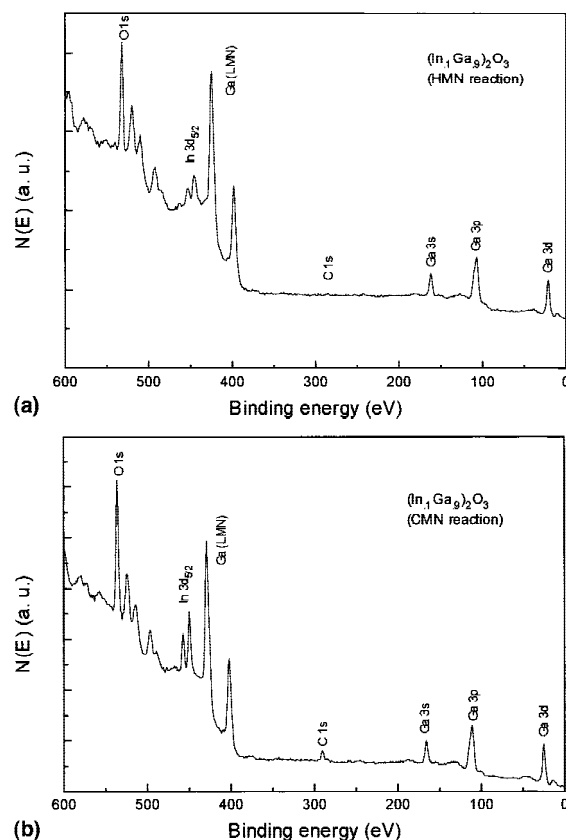
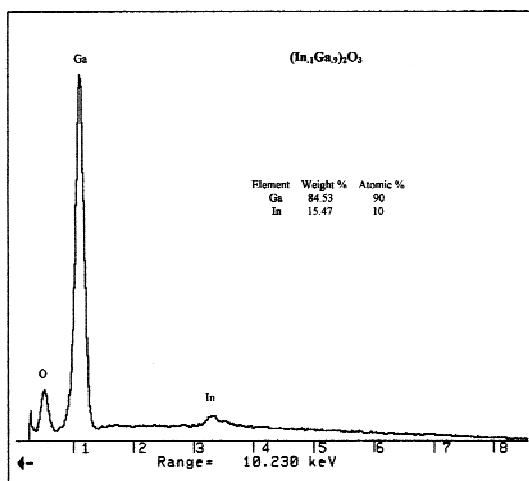


FIG. 7. (a) XPS spectra for  $(\text{In}_{0.1}\text{Ga}_{0.9})_2\text{O}_3$  powders synthesized by the hydrazine/metal nitrate method. (b) XPS spectra for  $(\text{In}_{0.1}\text{Ga}_{0.9})_2\text{O}_3$  powders synthesized by the carbohydrazide/metal nitrate method.

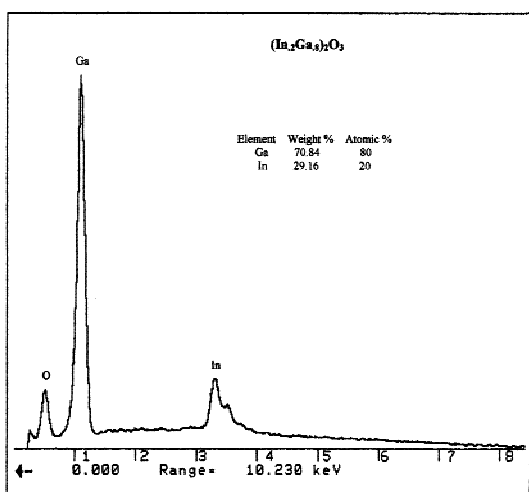
by CMN reaction. It can be seen that carbon is still present after cleaning the surface with  $\text{Ar}^+$  sputtering. The composition of the  $(\text{In}_{0.1}\text{Ga}_{0.9})_2\text{O}_3$  observed in the XPS analysis correspond to the composition calculated according to the chemical equation proposed for both methods.

Figures 8(a), 8(b), and 8(c) show the EDS spectra for  $(\text{In}_{0.1}\text{Ga}_{0.9})_2\text{O}_3$ ,  $(\text{In}_{0.2}\text{Ga}_{0.8})_2\text{O}_3$ , and  $(\text{In}_{0.3}\text{Ga}_{0.7})_2\text{O}_3$ , respectively. Three main peaks that correspond to oxygen, gallium, and indium are present, indicating that no impurities are found within the detection limit of the instrument. The insert tables in the figure show the atomic composition of each element in the sample. To quantify the In/Ga ratio in the powders, we assumed that powders composition  $x$  can be approximately obtained from the  $[\text{In}]/([\text{In}] + [\text{Ga}])$  ratio measured by EDS analysis. A mixed powders of  $\text{In}_2\text{O}_3$  and  $\text{Ga}_2\text{O}_3$  with 0.10, 0.20, and 0.30 mole fraction  $\text{In}_2\text{O}_3$ , which was weighed precisely and mixed fully, was used as a standard sample. The discrepancy of the  $[\text{In}]/([\text{In}] + [\text{Ga}])$  ratio between the mixture powders composition by weight and the

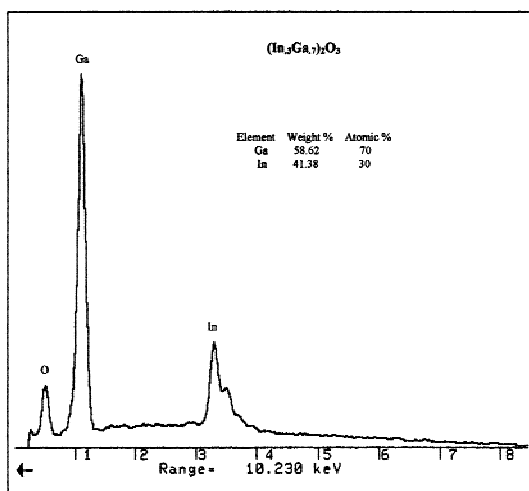




(a)



(b)



(c)

FIG. 8. (a) EDX spectrum for the  $(\text{In}_{0.1}\text{Ga}_{0.9})_2\text{O}_3$  powders synthesized by the hydrazine/metal nitrate method. (b) EDX spectrum for the  $(\text{In}_{0.2}\text{Ga}_{0.8})_2\text{O}_3$  powders synthesized by the hydrazine/metal nitrate method. (c) EDX spectrum for the  $(\text{In}_{0.2}\text{Ga}_{0.8})_2\text{O}_3$  powders synthesized by the hydrazine/metal nitrate method.

composition determined by EDS measurement was  $<1\%$ . Therefore, the accuracy of the powder composition  $x$  by this method is considered to be about  $1\%$ .

## CONCLUSIONS

A new combustion synthesis process for the bulk production of  $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$  with a higher purity, higher crystallinity, larger particle size has been reported here. Combustion synthesis using hydrazine ( $\text{N}_2\text{H}_4$ ) with metal nitrates was conducted in a controlled environment at low temperatures ( $<200^\circ\text{C}$ ).  $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$  powders were prepared by the carbohydrazide/nitrate metal reaction for comparison.

The results of x-ray diffraction showed a marked improvement in the crystallographic quality of the  $(\text{In}_x\text{Ga}_{1-x})_2\text{O}_3$  powders produced by hydrazine/metal nitrate method relative to that powder produced by carbohydrazide/metal nitrate method.

Scanning electron microscopy images of the  $(\text{In}_{0.1}\text{Ga}_{0.9})_2\text{O}_3$  powders produced by both methods show fine-scale porosity. The hydrazine/metal nitrate method produces particles in the as-synthesized state, whereas the carbohydrazide/metal nitrate method produces a reaction mass that must be crushed to form particles. The powder produced by the hydrazine/metal nitrate method showed an uniform particle-size distribution ( $3\text{--}6\ \mu\text{m}$ ), whereas the powder produced by the carbohydrazide/metal nitrate method had a foamy morphology.

X-ray photoelectron spectra showed a higher purity in the powder produced by hydrazine/metal nitrate method than those powders produced by carbohydrazide/metal nitrate method.

The results above indicates that the HMN reaction is excellent for the production of high-purity, chemically homogeneous, and well-crystallized powders.

This article presents a new route to synthesize low-temperature oxide compounds, which cannot be prepared by conventional methods and has significant technical importance in the synthesis of new and novel complex oxide.

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