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A NEW COMBUSTION SYNTHESIS TECHNIQUE FOR RARE EARTH-DOPED III-NITRIDE LUMINESCENT POWDERS

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A new low temperature method to produce $((RE)_xGa_{1-x})_2O_3$ ($1\geq x\geq 0$ and RE=Eu, Yb, Pr and Tm) powders with high purity, high chemical homogeneity and improved crystallinity has been developed. This procedure produces finely divided powders through an exothermic reaction between the precursors. The process starts with aqueous solutions of $RE(NO_3)_3$ and $Ga(NO_3)_3$ as the precursors and hydrazine as the (non-carbonaceous) fuel. The combustion reaction occurs when heating the precursors between 150 and 200°C in a closed vessel filled with an inert gas (Ar), which yields $(RE_xGa_{1-x})_2O_3$ directly. The preparation of RE-doped Ga_2O_3 powders was using a new combustion synthesis technique (Hydrazine / metal nitrate method). The preparation of Eu-doped GaN was using the ammonium hexafluoro-metal method. The powders were crystalline and high-purity as determined by XPS, EDS, SEM and XRD measurements.

1 Introduction

The rare earth-gallium oxide $[((RE)_xGa_{1-x})_2O_3]$ and rare earth-gallium nitride powders $[((RE)_xGa_{1-x})N]$ are luminescent materials and promising candidates for optoelectronic devices, low-cost solar cells with high efficiency, optical coatings, and various types of sensors[1, 2, 3].

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.

Combustion synthesis using hydrazine (N_2H_4) with metal nitrates was carried out in a controlled environment at low temperatures (< 200°C)[4].
Hahn and Juza[5] in 1940 introduced a method for the thermal decomposition of ammonium hexafluorogallate in streaming ammonia to obtain gallium nitride.
Nitriding process using ammonium hexafluoro-metals solid solutions was carried out in a tube reactor with controlled environment at 900°C.

In this work new methods for producing $((RE)_xGa_{1-x})_2O_3$ and GaN:RE powders with a high purity, high crystallinity and high homogeneity are presented.

2 Methods

The procedure for the combustion synthesis of $(RE_xGa_{1-x})_2O_3$ is illustrated in Fig. 1. The precursors were $RE(NO_3)_3{\bullet}XH_2O$, $Ga(NO_3)_3{\bullet}6H_2O$ and N_2H_4. The required mass of each reactant was calculated from the desired mass of the products, according to the chemical reactions. Once the reactor has been closed, an argon flow (500 ml/min) was supplied through the inlet valve to remove the air from the reactor and form an inert atmosphere. The heater was turned on. The ignition temperature which occurred between 150 – 200°C was measured with a thermocouple directly inserted into the beaker. Once the reaction had gone to completion, the beaker was removed from the reaction vessel and allowed to cool down to room temperature. The product (white powder) was removed from the beaker, placed into an agate mortar and ground with a pestle for approximately five minutes.

The procedure for the nitriding process, using ammonium hexafluoro-metal method, is illustrated in Fig. 2.

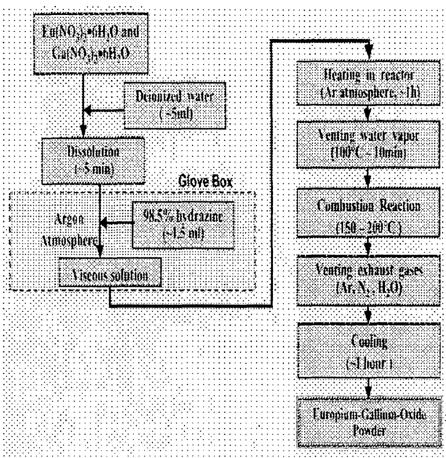

Fig. 1. Diagram of the Combustion Synthesis Process: Hydrazine/Metal Nitrate Method.

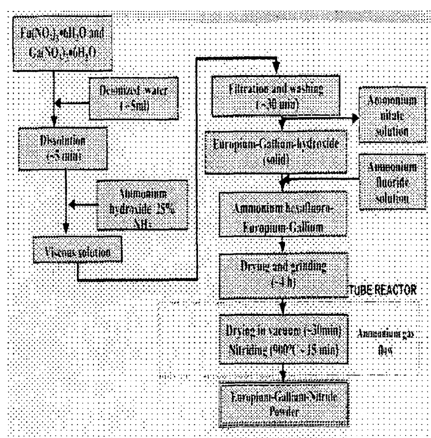

Fig. 2 . Diagram of Nitriding Process Ammonium Hexafluoro-Metal Method.

The morphology of the powders was studied with a scanning electron microscope (SEM) operated at 10 kV (Inserts in Fig. 3 and Fig. 4). The elemental composition of the powders (Fig. 5) was determined by means of X-ray photoelectron spectroscopy (XPS) employing an Mg anode with a characteristic X-ray energy of 1253.6 eV and Energy Dispersion Spectroscopy (EDS) (Fig. 3 and Fig. 4). The powders crystallinity was determined by X-Ray Diffraction (XRD) (Fig. 6).

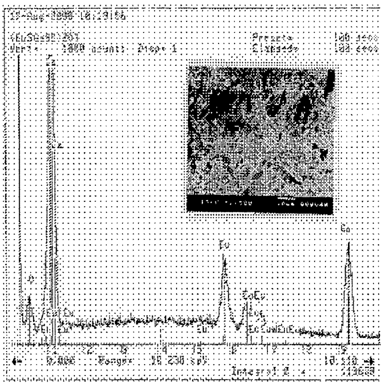

Fig. 3. EDS spectra and SEM micrograph of $(Eu_{0.05}Ga_{0.95})_2O_3$ powders.

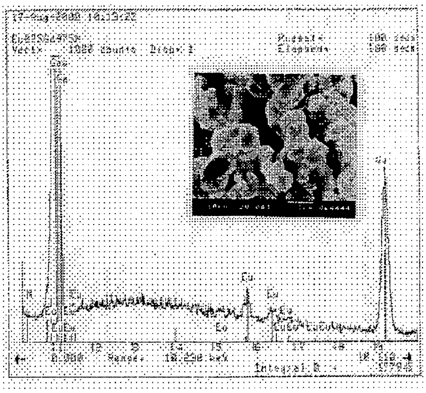

Fig. 4. EDS spectra and SEM photo of $(Eu_{0.025}Ga_{0.975}N)$ powders.

The morphology of the powders was studied with a scanning electron microscope (SEM) operated at 10 kV (Inserts in Fig. 3 and Fig. 4). The elemental composition of the powders (Fig. 5) was determined by means of X-ray photoelectron spectroscopy (XPS) employing an Mg anode with a characteristic X-ray energy of 1253.6 eV and Energy Dispersion Spectroscopy (EDS) (Fig. 3 and Fig. 4). The powders crystallinity was determined by X-Ray Diffraction (XRD) (Fig. 6).

3 Discussion and Conclusions

Combustion synthesis process (Hydrazine/metal nitrate method) produces Eu-doped Ga_2O_3 luminescent powders in a controlled environment with large particle size ranging between 5 and 10 μm with poor crystallinity and high purity.
Nitriding process (Ammonium hexafluoro-metal method) proceeds Eu-doped GaN powders with poor luminescence, high purity (EDS and XPS) and crystallinity (XRD), small particle size, between 0.5 and 1 μm.

A new combustion synthesis process for bulk production of Eu-doped Ga_2O_3 luminescent powders has been developed. This process presents the following advantages:

- Low temperature process (starting at temperatures <200 °C).
- Production of large particle size (between 5 – 10 μm)
- Production of powders with high purity
- Production of crystalline materials

A new nitriding method for bulk production of Eu-doped GaN powders has been developed. This process has the following characteristics:

- Production of small particle size (between 0.5 – 1 μm
- Production of crystalline materials with high purity.

Both methods can be used to produce other complex oxides and nitrides.

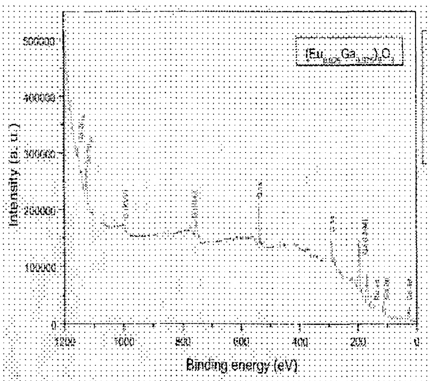

Fig. 5. XPS spectra of $(Eu_{0.025}Ga_{0.975})_2O_3$ made by the hydrazine/metal nitrate method.

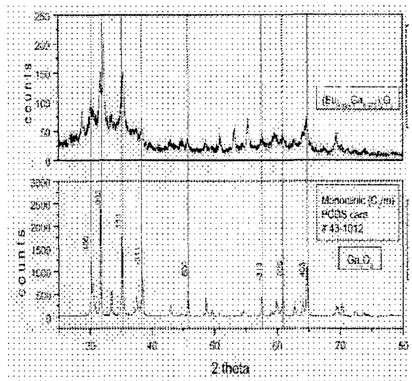

Fig. 6. XRD spectra of $(Eu_{0.025}Ga_{0.975})_2O_3$ and Ga_2O_3 powders.

4 Acknowledgements

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