

## A New Combustion Synthesis Method for GaN:Eu<sup>3+</sup> and Ga<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> Luminescent Powders

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New low-temperature methods to produce GaN:Eu and Ga<sub>2</sub>O<sub>3</sub>:Eu ( $0 \leq x \leq 1$ ) highly-luminescent powders are presented. These procedures yield finely divided powders through exothermic reactions between the precursors. The preparation of Eu-doped Ga<sub>2</sub>O<sub>3</sub> powders was achieved using a new combustion synthesis technique (hydrazine/metal-nitrate method). The process starts with aqueous solutions of Eu(NO<sub>3</sub>)<sub>3</sub> and Ga(NO<sub>3</sub>)<sub>3</sub> as the precursors and hydrazine as (non-carbonaceous) fuel. A spontaneous combustion reaction occurs by increasing the temperature to between 150 and 200 °C in a closed vessel filled with argon, and produces (Eu<sub>x</sub>Ga<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> directly. The preparation of Eu-doped GaN uses the ammonium hexafluoro-metal method. The powders present strong luminescence associated with the dopant. A sharp and strong GaN luminescence is observed, indicative of high purity and crystallinity as determined by low-temperature cathodoluminescence. The composition and powder morphology have been studied using energy dispersive spectroscopy and scanning electron microscopy.

**Introduction** Luminescence from rare earth-doped materials has generated much interest in recent years. In particular, rare earth-gallium oxide [((RE)<sub>x</sub>Ga<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub>] and rare earth-doped gallium nitride [((RE)<sub>x</sub>Ga<sub>1-x</sub>)N] are luminescent materials and promising candidates for optoelectronic devices, low-cost solar cells with high efficiency, optical coatings and various types of sensors [1–3]. The mechanism for combustion synthesis has been studied during the last decade. It has been found that the combustion process is controlled by the heating rate, the fuel to oxidizer ratio, the type of fuel, the ignition temperature and the volume of precursors. Combustion synthesis using hydrazine (N<sub>2</sub>H<sub>4</sub>) with metal nitrates has been carried out in a controlled environment at low temperatures (<200 °C) [4]. Hahn and Juza in 1940 developed a method for the thermal decomposition of ammonium hexafluorogallate in streaming ammonia to obtain gallium nitride [5]. In this work, new methods to obtain GaN:Eu and (Eu<sub>x</sub>Ga<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> luminescent powders with a high purity, high crystallinity and high homogeneity are presented. The nitriding process using ammonium hexafluoro-metal solid solutions was carried out in a cylindrical reactor in a controlled environment, at 900 °C.

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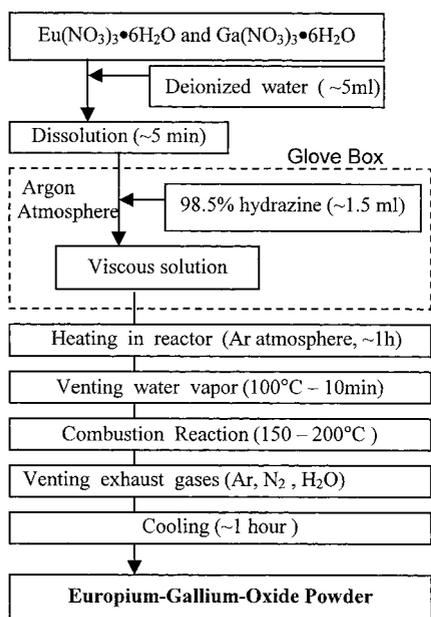


Fig. 1

Fig. 1. Flow diagram for the combustion synthesis process for  $\text{Ga}_2\text{O}_3:\text{Eu}^{3+}$

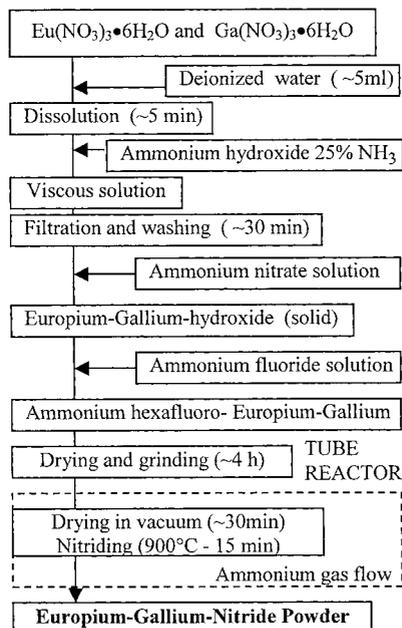


Fig. 2

Fig. 2. Flow diagram of the nitriding process for  $\text{GaN}:\text{Eu}^{3+}$

**Experimental Details** The procedure for the combustion synthesis of  $(\text{Eu}_x\text{Ga}_{1-x})_2\text{O}_3$  is illustrated in Fig. 1. The precursors were  $\text{Eu}(\text{NO}_3)_3 \cdot \text{XH}_2\text{O}$ ,  $\text{Ga}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{N}_2\text{H}_4$ . The required mass of each reactant was calculated from the desired mass of the products, according to the chemical reactions. Once the reactor had been closed, an argon flow (500 sccm) 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 occurred between 150 and 200 °C and 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 an ammonium hexafluoro-metal method, is illustrated in Fig. 2. A detailed description is reported elsewhere [6].

**Results and Discussion** Figures 3 and 4 show the chemical composition of the luminescent powders analyzed by energy dispersive X-ray spectroscopy (EDS). No impurities (e.g. carbon) are observed, indicative of the high-purity of these materials.

The morphology of the powders was observed with a scanning electron microscope (SEM) operated at 10 kV (right portion of Figs. 3 and 4). These observations clearly show that the surface of  $\text{Ga}_2\text{O}_3:\text{Eu}^{3+}$  is composed of particles ranging between 5 and 10  $\mu\text{m}$  while the particle size for  $\text{GaN}:\text{Eu}^{3+}$  lies within the 0.5–1.0  $\mu\text{m}$  range.

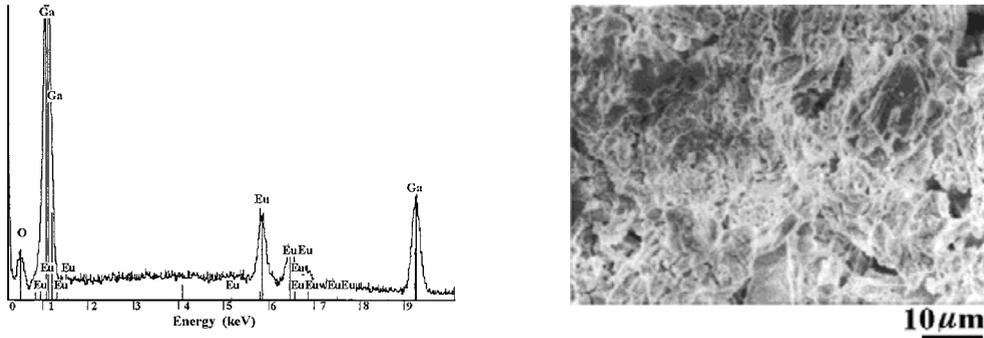


Fig. 3. EDS (left) and SEM (right) of Ga<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> powders

A representative cathodoluminescence emission spectrum of GaN:Eu<sup>3+</sup> powders is shown in Fig. 5. The GaN emission at 360 nm is relatively strong for powders of this type, and its sharpness is clear indication of high crystallinity and chemical purity of the GaN matrix.

The main Eu<sup>3+</sup> transition at 611 nm corresponds to <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub> transition of the f shell, which is a known laser transition [6, 7] for Eu<sup>3+</sup>. The excited levels <sup>5</sup>D<sub>1</sub> and <sup>5</sup>D<sub>0</sub> most frequently luminesce with emission from <sup>5</sup>D<sub>0</sub> more prevalent than emission from any other <sup>5</sup>D<sub>J</sub> level. Therefore, the minor peaks in the spectrum of Fig. 5 are believed to be transitions from <sup>5</sup>D<sub>1</sub> and <sup>5</sup>D<sub>0</sub> to the <sup>7</sup>F<sub>J</sub> (J = 1, 2, 3) levels, which is in good agreement with values reported in the literature [7].

**Conclusions** New fabrication methods of highly luminescent GaN:Eu and Ga<sub>2</sub>O<sub>3</sub>:Eu powders have been reported here. The first is a new combustion synthesis process for bulk production of Eu-doped Ga<sub>2</sub>O<sub>3</sub> luminescent powders. This is a low temperature process (starting temperatures <200 °C), which yields large particle size (between 5 and 10 μm in diameter) of high purity crystalline powder. The second is a new nitriding method for the fabrication of Eu-doped GaN powders. This process yields smaller particle size (ranging between 0.5 and 1 μm) of high-crystallinity and high-purity luminescent materials. The method described here is a versatile way to produce luminescent powders for the fabrication of robust targets for physical vapor deposition of lumines-

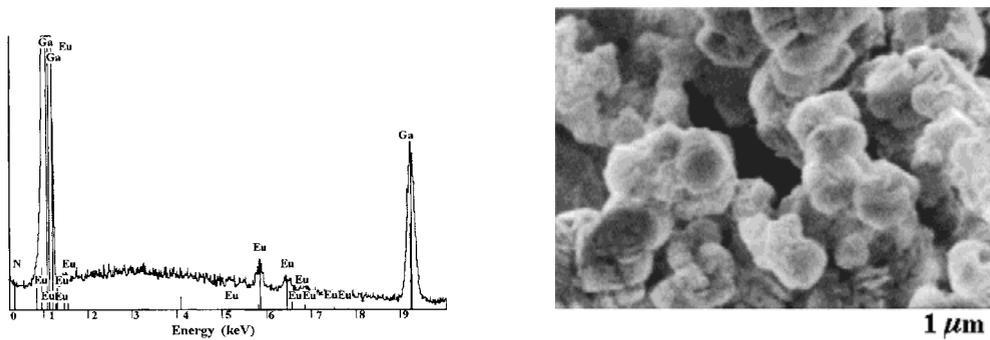


Fig. 4. EDS (left) and SEM (right) of GaN:Eu<sup>3+</sup> powders

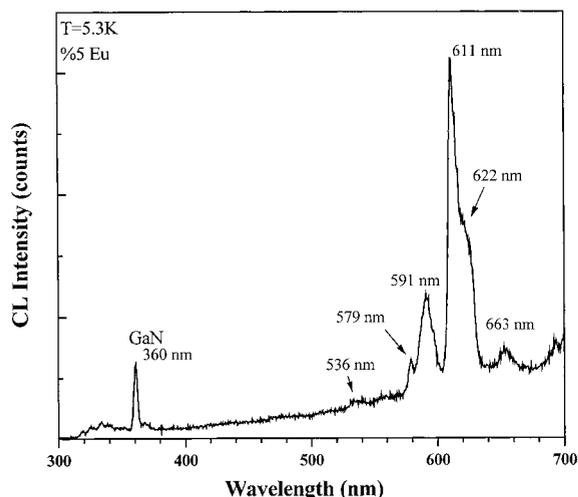


Fig. 5. Cathodoluminescence emission of the GaN:Eu<sup>3+</sup> powders excited with a 5 keV electron

cent GaN:Eu thin films (i.e. by magnetron sputtering and by pulsed laser ablation). Both methods can be used to obtain other rare earth-doped (e.g., Er, Pr, Tb) III-oxides and III-nitrides.

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## References

- [1] S. STRITE and H. MORKOC, *J. Vac. Sci. Technol. B* **10**, 1237 (1992).
- [2] F. A. PONCE and D. P. BOUR, *Nature* **386**, 351 (1997).
- [3] A. J. STECKL and J. M. ZAVADA, *MRS Bull.* **24**, 33 (1999).
- [4] R. GARCIA, G. A. HIRATA, and J. MCKITTRICK, *J. Mater. Res.* **16**, 1059 (2001).
- [5] H. HAHN and R. JUZA, *Z. Anorg. Allgem. Chem.* **244**, 111 (1940).
- [6] R. GARCIA, G. A. HIRATA, M. H. FARIAS, and J. MCKITTRICK, *Mater. Sci. Eng. B*, in press (2001).
- [7] R. REISFELD and C. K. JORGENSEN, in: *Lasers and Excited States of Rare Earths*, North Holland Publ. Co., New York 1978 (pp. 93–94).