

# Synthesis of rare-earth activated AlN and GaN powders via a three-step conversion process

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Using a three-step solution method, we have successfully synthesized rare-earth (RE) activated AlN, GaN, and pure GaAlN powders. Aluminium and/or gallium nitrates are first dissolved in water. For AlN:RE, rare-earth nitrates converted from their corresponding oxides of Dy<sup>3+</sup> and Tm<sup>3+</sup> are then added to the precursor nitrate solution. The mixture is subsequently converted into Al(OH)<sub>3</sub>:RE by combining with aqueous NH<sub>4</sub>OH at room temperature. The product is then mixed with aqueous NH<sub>4</sub>F to form (NH<sub>4</sub>)<sub>3</sub>AlF<sub>6</sub>:RE. The conversion process is complete when the hexafluoride compound is

flushed with anhydrous ammonia to produce the final nitride product AlN:Dy<sup>3+</sup>,Tm<sup>3+</sup>. GaN, GaN:Tb<sup>3+</sup> and GaAlN are synthesized similarly. Single phase, pure GaN and GaAlN formation has been confirmed. Dysprosium oxide has been observed in AlN:Dy<sup>3+</sup>, Tm<sup>3+</sup>. Oxygen concentration of approximately 4 at% has been measured in GaN powders, and is slightly higher in AlN powders. Spectroscopic measurements show clearly observable emission from Dy<sup>3+</sup> and Tm<sup>3+</sup> co-activated AlN samples. In activated GaN samples, Tb<sup>3+</sup> emission has been observed.

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**1 Introduction** Research in wide band gap nitride semiconductors such as AlN, GaN and InN has received increased attention due to their application in optoelectronic devices. Their alloys yield nitrides with a tunable band gap across the visible spectrum from red (1.9 eV) to ultra-violet range (6.2 eV), suitable for application in solid-state lighting [1]. While single color emission can be achieved by nitride alloys, multiple color emission has been achieved by activating GaN thin films with rare earth ions such as Eu<sup>3+</sup>, Er<sup>3+</sup> and Tm<sup>3+</sup> with the potential for white light emission [2]. Techniques for depositing nitride thin films include metal-organic chemical vapor deposition (MOCVD) [3], metal-organic vapor phase epitaxy (MOVPE) [4] or molecular beam epitaxy (MBE) [5]. As a preliminary step, however, powder synthesis provides a more economical approach and a rapid alternative for studying material properties and designing novel materials systems prior to thin film deposition. Furthermore, powder

synthesis requires simpler equipment and is particularly suitable for investigating optical and luminescence properties due to enhanced scattering from the particle surfaces. Recently, various groups have demonstrated activator emission in bulk GaN powders. Blue emission was demonstrated by Ogi et al. with their GaN:Mg powders [6], while green emission from Er<sup>3+</sup> activated GaN powders was observed by Wu et al. [7]. Nyk et al. also showed Eu<sup>3+</sup> and Tb<sup>3+</sup> emission separately in GaN host [8]. Due to an incompletely filled 4f shell that is shielded by the filled 5s<sup>2</sup> and 5p<sup>6</sup> orbitals, the f → f transitions in a rare-earth (RE) ion are largely unaffected by the host lattice [9]. Since Dy<sup>3+</sup>, Tm<sup>3+</sup> and Tb<sup>3+</sup> are also common RE ions often used in phosphors such as Y<sub>2</sub>O<sub>3</sub> and Y(P,V)O<sub>4</sub> as yellow, blue and green luminescent ions respectively [10], we have chosen to study these ions in the nitride host.

In this work, we report the synthesis and luminescence measurement of RE activated AlN and GaN synthesized by

a solution-based method. The same method has also been used to synthesize pure GaAlN powders, and high purity GaN. The synthesis process has been described briefly elsewhere [11], with modifications to the starting material and experimental parameters as originally reported. Starting with nitrate precursors, the reaction products were sequentially converted to hydroxides, hexafluorides, and finally nitrides. Phase identification was performed by X-ray diffraction (XRD), and elemental compositions including the oxygen content of the powders were determined by energy dispersive spectroscopy (EDS). Cathodoluminescence (CL) measurements were also performed to determine the emission spectra of the powders.

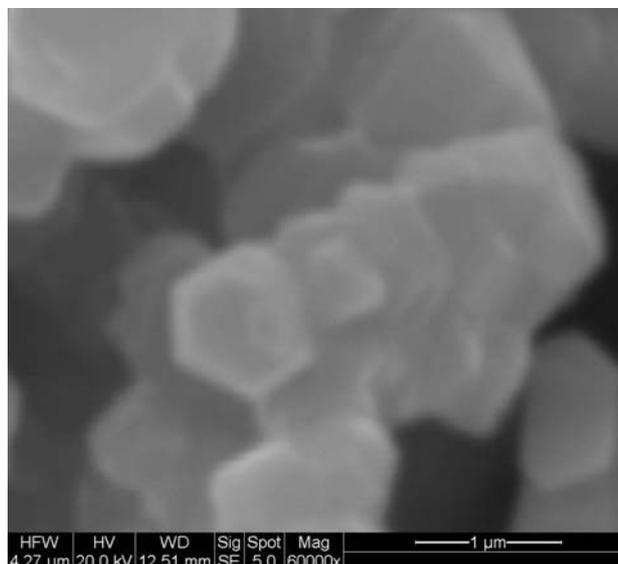
**2 Experimental** For AlN:Dy<sup>3+</sup>,Tm<sup>3+</sup>, the activator oxides Dy<sub>2</sub>O<sub>3</sub> and Tm<sub>2</sub>O<sub>3</sub> were weighed in 1:1 ratio and dissolved in concentrated nitric acid to form their corresponding nitrates. These were added to an aqueous solution of aluminium nitrate and water in a molar ratio to ultimately form 1 at% Dy<sup>3+</sup> and 1 at% Tm<sup>3+</sup> in AlN. The solution was converted to hydroxide, fluoride, and finally nitride as discussed elsewhere [8]. For GaN:Tb<sup>3+</sup>, Ga(NO<sub>3</sub>)<sub>3</sub> and Tb(NO<sub>3</sub>)<sub>3</sub> were used directly as purchased (Puratronic, Alfa-Aesar). The same procedure as described above was followed. GaN and GaAlN were prepared similarly using Ga(NO<sub>3</sub>)<sub>3</sub> and a mixture of Ga(NO<sub>3</sub>)<sub>3</sub> and Al(NO<sub>3</sub>)<sub>3</sub> as starting materials in a 9:1 and 4:1 ratio for Ga<sub>0.9</sub>Al<sub>0.1</sub>N and Ga<sub>0.8</sub>Al<sub>0.2</sub>N, respectively.

**3 Results and discussion** With ~300mg of fluoride precursor, ~60mg of AlN:RE and ~120mg of GaN, GaN:RE and GaAlN product could be synthesized. SEM micrographs clearly show submicron-sized, hexagonal particles (Fig. 1).

While EDS measurements as shown in Table 1 indicate significant oxygen content in AlN samples, it is likely due to the formation of additional phases including Dy<sub>2</sub>O<sub>3</sub> as observed in XRD measurements (Fig. 2). Oxygen content is much lower in GaN samples. Relative to commercial GaN powders (Alfa-Aesar), the samples prepared by the current method contains significantly lower oxygen content.

GaN powders were matched to JCPDS card number 00-050-0792 and AlN powders were matched to JCPDS card number 00-025-1133, confirming their wurtzite structure. Si powder was mixed in the samples during XRD measurements for calibration purposes. No additional phase was identified in GaN or GaAlN samples. To calculate the amount of aluminium incorporation, the XRD pattern of the GaAlN powder was compared with the reference JCPDS card. The peak position shift in the XRD pattern (Fig. 3) was used in Vegard's law [12] to calculate the aluminium content. More significant peak shift was observed in nitrogen-dried sample, which contained 18% calculated aluminium versus 9% calculated aluminium for air-dried sample. This suggested that the drying atmosphere

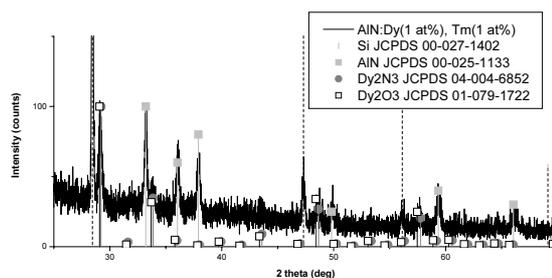
influences the nitride alloy content with the presence of nitrogen favoring aluminium incorporation.



**Figure 1** SEM micrograph showing sub-micron size, hexagonal AlN particles.

**Table 1** Oxygen content of nitride samples.

Composition	Average oxygen content (at% ± stdev)	O/N Ratio
AlN:Dy(1 at%), Tm(1at%)	5.86 ± 1.77	0.148
GaN:Tb(1 at%)	3.43 ± 0.76	0.092
GaN	3.73 ± 2.02	0.083
Commercial GaN	10.78 ± 3.15	0.290



**Figure 2** XRD pattern of AlN:Dy(1 at%) and Tm(1 at%) showing presence of Dy<sub>2</sub>N<sub>3</sub> and Dy<sub>2</sub>O<sub>3</sub> phase. Vertical dash lines correspond to Si JCPDS card.

