Mg²⁺-Doped GaN Nanoparticles as Blue-Light Emitters: A Method to Avoid Sintering at High Temperatures

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Bright blue-light emission at 410 nm is observed from Mg²⁺-doped GaN nanoparticles prepared by the nitridation of Ga₂MgO₄ nanoparticles at 950°C. The sintering of these nanoparticles during high-temperature nitridation was prevented by mixing the Ga₂MgO₄ precursor nanoparticles with La₂O₃ as an inert matrix before the nitridation process. The Mg²⁺-doped GaN nanoparticles were isolated from the matrix by etching with 10% nitric acid. The Mg²⁺-doped GaN nanoparticles were characterized by photoluminescence, atomic force microscopy, X-ray diffraction, and IR analyses.

Keywords:
- blue-light emitters
- doping
- gallium nitride
- nanoparticles

1. Introduction

Nanomaterials made of III–V semiconductors in general and GaN in particular as blue- or ultraviolet-light emitters have attracted a great deal of research interest as they are potential candidates for making light-emitting diodes (LEDs), lasers and optical amplifiers, electroluminescent devices, field-effect transistors (FETs), and so on.[1–3] Thin films of GaN are widely studied and generally prepared by techniques such as metal-organic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE).[4,5] These thin films are primarily used in the fabrication of blue and ultraviolet LEDs.[6,7] Blue is one of the primary colors used in white-light panel displays and hence materials that are sources of blue light are technologically important.[8] For instance, blue and UV LEDs have great prospect as light sources because they would increase the data-storage capacities in compact discs (CDs) and digital video discs (DVDs). Despite the application of organic electroluminescent devices in making blue and white OLEDs, their low efficiency and stability calls for the use of very robust materials such as GaN.[9,10] Blue-light emission has been observed from Mg²⁺-, Tm³⁺- and As-doped GaN films and nanowires.[11–13] Lee and Steckl have observed enhanced blue-light emission from Tm³⁺-doped AlGaN electroluminescent devices (EL).[14] Most of the GaN-based devices made so far are based on GaN films.[15,16] However, the main disadvantages of these inorganic thin-film LEDs are their mechanical properties, which prevent them from convenient fabrication into any desired shape, as well as their high fabrication cost. An alternative to this could be the incorporation of GaN nanoparticles in polymer-based LEDs as they can be fabricated into any shape or size using cheaper fabrication methods, such as spin coating.

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There are only a few reports available on the blue-light emission from GaN-based nanomaterials. For example, the thermal decomposition of an amido precursor $[Ga_2(NMe_2)_6]$ in NH_3 resulted in the formation of a polymeric intermediate, which on reaction with NH_3 resulted in GaN nanoparticles.[17] Recently, van Patten et al. discovered that the same precursor can be used to produce GaN nanocrystals without the use of NH_3.[18] The same group reported very recently a room-temperature synthesis of GaN from Li_3N and $GaCl_3$ that emits at 320 nm, which shifted to 365 nm upon annealing at 310°C.[19] Solvothermal decomposition of a $GaCl_3$ and NaN_3 mixture and in situ thermal decomposition of cyclotrigallazane incorporated into a polymer results in the formation of GaN nanoparticles that exhibit blue-light emission near 426 and 475 nm, respectively.[20,21] The origin of the blue-light emission is mainly attributed to the presence of impurity or defect levels, which is less desirable, because they are often difficult to control. Moreover, the syntheses of many of these GaN nanoparticles involve the use of azides or other organometallic reagents as precursors for gallium and nitrogen, which are highly explosive, very toxic, and extremely sensitive to air requiring the reactions to be performed with extreme care in a glove box. We would like to stress here that quantum-size effects would shift the band-edge emissions of nanoparticles further into the UV compared to the bulk bandgap of 3.34 eV (371 nm) and thus does not provide a strategy to obtain blue-light emission. Alternatively, lanthanide-doped GaN nanomaterials are advantageous as they have characteristic narrow emission lines that fall anywhere from the visible to the NIR region. Due to the large size mismatch between Ln^{3+} and Ga^{3+}, only very few reports are available on lanthanide-doped GaN nanomaterials.[22–24] Though the incorporation of Eu^{3+} and Er^{3+} ions into nanopowders of GaN leads to red- and green-light emissions, respectively, blue-light emission remains challenging. Our attempts to incorporate corresponding blue-light-emitting lanthanide ions such as Tm^{3+} or Dy^{3+} into a GaN matrix did not lead to blue-light emission, possibly due to quenching by surface defects.

In the present study, we report the synthesis of Mg^{2+}-doped GaN nanoparticles, which exhibit strong blue-light emission around 410 nm. These nanoparticles were prepared by the nitridation of Ga_2MgO_4 nanoparticles at 950°C in an ammonia atmosphere. The high temperature employed in the preparation usually leads to sintering of the GaN nanoparticles thus hindering the post-chemical treatment to improve their processability in organic medium. To circumvent this problem we developed an easy method in which the precursor Ga_2MgO_4 nanoparticles were first diluted in an inert matrix before the nitridation reaction. This is achieved by mixing the precursor nanoparticles with Eu^{3+}-doped La_2O_3 matrix in the ratio of 1:10. Eu^{3+} was used as an optical probe to understand if any changes occurred in the matrix during the nitridation step. After nitridation, the Mg^{2+}-doped GaN nanoparticles were separated from the matrix by dissolving the matrix and some formed MgO completely with 10% aqueous HNO_3. The optical properties of the Mg^{2+}-doped GaN nanoparticles were not affected by the nitric acid treatment. These nanoparticles were coated with trioctylphosphine oxide (TOPO) to improve their dispersibility in organic solvents.

2. Results and Discussion

Scheme 1 illustrates the various steps involved in the synthesis of Mg^{2+}-doped GaN nanoparticles. First, the Ga_2MgO_4 nanoparticles prepared by combustion were
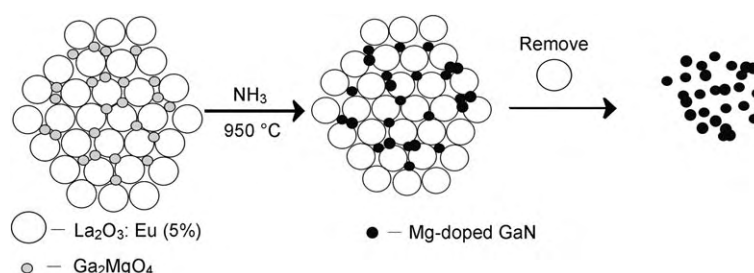
Scheme 1. Schematic representations of the various steps involved in the preparation of Mg^{2+}-doped GaN nanoparticles in an inert matrix.

mixed with a La_2O_3 matrix at a mass ratio of 1:10. These oxide mixtures were then exposed to NH_3 atmosphere at 950°C for 3 h. This resulted in the formation of Mg^{2+}-doped GaN nanoparticles, which were subsequently separated from the matrix by removing the matrix with 10% nitric acid.

The Ga_2MgO_4 nanoparticles were prepared using the combustion method.[25,26] During the combustion synthesis, a highly exothermic reaction between the oxidant (nitrate ions) and fuel (glycine) results in localized heating, thereby forming the nanoparticles without much sintering. X-ray diffraction (XRD) patterns of the nanoparticles revealed the formation of Ga_2MgO_4 and atomic force microscopy (AFM) analysis indicates that the average particle size is approximately 6 nm. A typical AFM image and XRD pattern are shown in Figures S1 and S2 of the Supporting Information, respectively.

Figure 1 shows the emission spectra for Mg^{2+}-doped GaN nanoparticles before and after removal of the matrix. The emission spectrum of Mg^{2+}-doped GaN before removal of the matrix exhibits a strong peak at 410 nm along with some sharp emission peaks at 578, 591, and 619 nm. The latter three peaks arise from the Eu^{3+} ions that are doped inside the La_2O_3 matrix (see further). These sharp peaks are assigned to the $^5D_0 \rightarrow {}^7F_{0,1,2}$ transitions, respectively.[27] After nitric acid treatment, the sharp emission peaks corresponding to the Eu^{3+} emissions are absent, indicating the com-
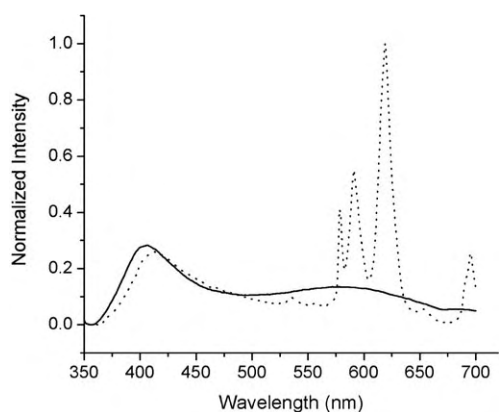
Figure 1. Normalized emission spectra of Mg²⁺-doped GaN nanoparticles before (dashed trace) and after (solid trace) removal of the Eu³⁺-doped La₂O₃ matrix.

Figure 2. Experimental (dotted trace) and calculated (solid trace) X-ray diffraction pattern of Mg²⁺-doped GaN nanoparticles after removal of the La₂O₃ inert matrix and MgO. The small peaks at the left, from left to right, are cristobalite, most likely from the quartz tube in the tube furnace, and some remaining La₂O₃, respectively.

plete removal of the matrix. This also indicates that no Eu³⁺ ions diffused into the GaN material during the nitridation step. The emission peak at 410 nm is retained with a less intense broad band around 580 nm. The emission observed around 410 nm is from Mg²⁺-doped GaN. To verify that the emission is originating from Mg²⁺ doping in the GaN matrix, we prepared GaN nanoparticles without magnesium doping under identical conditions. This sample exhibits a sharp emission near 385 nm, which is attributed to band-edge emission.[24,28] For comparison, the emission spectrum of GaN along with that of Mg²⁺-doped GaN nanoparticles are displayed in Figure S3. The emission spectrum collected from Mg²⁺-doped GaN nanoparticles is red-shifted by 25 nm. This shift is attributed to the Mg²⁺ doping of the GaN matrix. The emission of the Mg²⁺-doped GaN nanoparticles is much stronger than of the GaN nanoparticles.

Blue-light emission has been reported for Mg²⁺-doped GaN thin films around 450 nm, which can be ascribed to the donor–acceptor-pair recombination.[29–31] It is suggested that the acceptor is an isolated Mg$_{Ga}$ (magnesium at a gallium site) and the donor is attributed to a Mg$_{Ga}$ acceptor with a nitrogen vacancy.[19] We retain a similar explanation for the origin of the 410-nm emission. It is quite possible that the differences in fabrication of the thin films and our nanoparticles have a subtle, yet distinct effect on the photoluminescence. The broad emission centered at 580 nm is assigned to the well-known yellow emission from GaN. The origin of this emission is, however, still under debate.[31–33] It is most likely due to the presence of intrinsic defects in the GaN lattice. Recently, Kudrawiec et al. observed yellow-light emission in Eu³⁺-doped GaN powders. They have demonstrated that the yellow-light emission is associated with surface-related defects.[16] The intensity of this emission is dominant in nanometer-sized grains compared to micrometer-sized grains. The presence of this yellow-light emission in our sample suggests that the grain sizes are in the nanometer range (see below).

The formation of the pure wurtzite phase of GaN is indicated by the XRD pattern displayed in Figure 2. The peaks appearing at the 2θ values of 33, 35, and 37 are respectively assigned to the (100), (002), and (101) peaks of the nano-
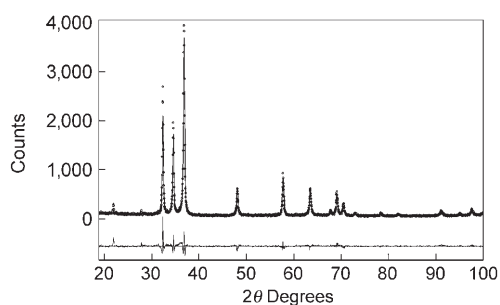
crystalline GaN. The lattice parameters [$a = 3.18298$ (47); $c = 5.17706$ (93)] for undoped GaN increased to [$a = 3.19217$ (55); $c = 5.18476$ (93)] for Mg-doped GaN. This slight increase in the lattice parameters can be attributed to the incorporation of magnesium ions in GaN at a Ga³⁺ site or an interstitial site. There could be two reasons: first, the incorporation of Mg²⁺ (0.58 Å) having a larger ionic radius compared to Ga³⁺ (0.47 Å) would lead to an increase in the lattice. Secondly, incorporation of Mg²⁺ would lead to nitrogen vacancies thus expanding the lattice. The reason for only a slight increase might be attributed to chemical interaction between the magnesium and the nitrogen atoms. This reduces their volume, which would restrict the lattice expansion.[34] In the Mg²⁺-doped GaN samples prepared without the La₂O₃ matrix we observed a 5% MgO (periclase) phase in the XRD pattern (Figure S4). This implies that some MgO had formed as a separate phase. This phase separation must have happened during the nitridation step. The absence of observation of any MgO phase for the Mg²⁺-doped GaN nanoparticles prepared with the La₂O₃ matrix indicates that the nitric acid treatment employed to remove the La₂O₃ matrix etches the MgO away as well. The formation of the GaN and the complete removal of the matrix (Eu³⁺-doped La₂O₃) after nitric acid treatment are also substantiated by IR measurements (Figure 3). The presence of
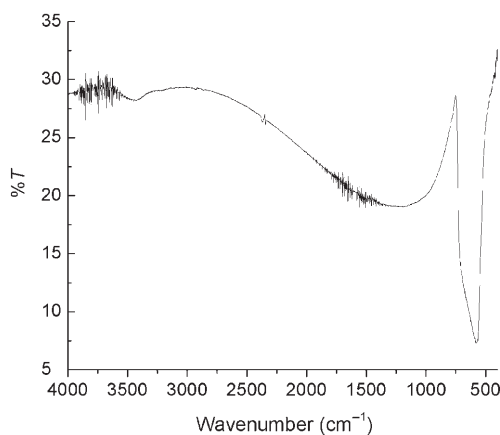

Figure 3. FT-IR spectrum of the Mg²⁺-doped GaN nanoparticles after removal of the Eu³⁺-doped La₂O₃ matrix and MgO.

strong stretching at 575 cm^{-1}, characteristic of Ga-N, and no peaks corresponding to the lanthanum oxide matrix are observed. The presence of magnesium in the Mg^{2+}-doped GaN nanoparticles after the nitric acid treatment was verified by energy dispersive X-ray spectroscopy (EDS) (Figure S5). The EDS results indicate that the ratio of Ga to Mg is close to 16:1 suggesting a doping level of approximately 6.0% Mg in GaN. This ratio is very close to the expected value calculated from the weight percent of magnesium in Ga$_2$MgO$_4$ nanoparticles and taking into account the 5% MgO phase that was formed during the nitridation (see before).

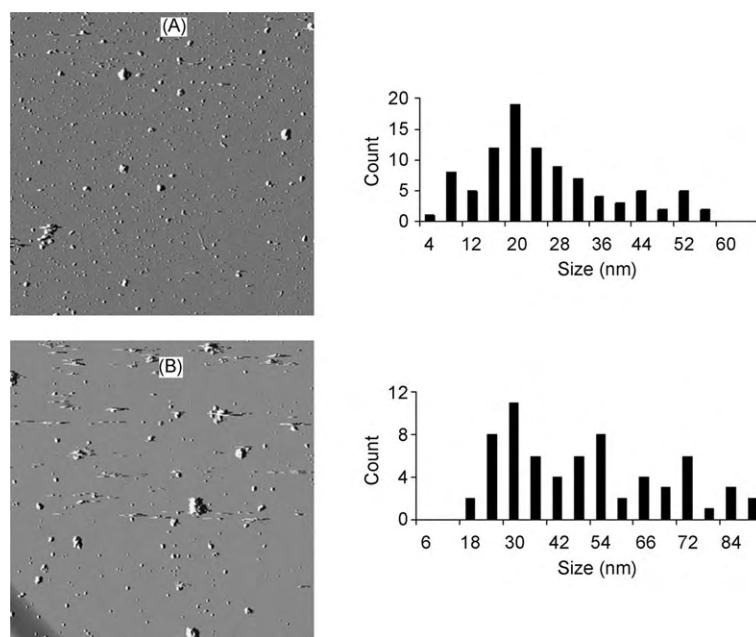The absence of any remarkable change in the La$_2$O$_3$ matrix during the ni-

Figure 4. AFM images of the TOPO-coated Mg^{2+}-doped GaN nanoparticles that are prepared with (A) and without (B) the matrix, and their corresponding size histograms. The AFM image dimensions are 50 μm × 50 μm.

tridation of Ga$_2$MgO$_4$ was confirmed by the emission analysis. No change in the Eu^{3+} emission pattern, which is very sensitive to the environment, was observed for the as-prepared Eu^{3+}-doped La$_2$O$_3$ and after nitridation in NH$_3$ at 950°C (Figure S6). This is further supported by the XRD studies, which indicate hardly any change in the La$_2$O$_3$ patterns before and after nitridation at 900°C (not shown).

To study the effect of using a matrix in avoiding the sintering of nanoparticles during high-temperature nitridation, after removal of the matrix the Mg^{2+}-doped GaN nanoparticles were coated with trioctylphosphine oxide (TOPO) to improve their dispersibility in organic medium. Ligand-stabilized nanoparticles are important for the fabrication of polymer-based LED devices. There are hardly any reports available on the synthesis of ligand-stabilized GaN nanoparticles. Micic et al. demonstrated the synthesis of GaN quantum dots coated with a mixture of trioctylamine/hexadecylamine (TOA/HDA) where HDA was used to improve the hydrophobicity of the quantum dots.[35] Recently, Sardar and Rao have shown the synthesis of cetyltrimethylammonium bromide (CTAB)-capped GaN nanocrystals from organometallic precursors such as gallium cupferron (Ga-(C$_6$H$_5$N$_2$O$_2$)$_3$) under solvothermal conditions.[36] We used TOPO in a subsequent step as a coordinating ligand for the GaN nanoparticles. The attachment of TOPO to the surface of the GaN particles is verified by IR analysis (Figure S7: a strong C–H stretch absorption is observed, in addition to a weak signal at 1125 cm^{-1} for the P=O stretching frequency). AFM images of the TOPO-coated Mg^{2+}-doped GaN nanoparticles that were prepared with and without a La$_2$O$_3$ matrix are shown in Figure 4. The images clearly substantiate that the Mg^{2+}-doped GaN nanoparticles prepared with

a matrix show much less sintering compared to the nanoparticles prepared without a matrix. Though some aggregation of nanoparticles is observed for the synthesis in the matrix, it is much less compared to the GaN particles prepared without the La$_2$O$_3$ matrix. This is substantiated by the histogram analysis which is shown on the right-hand side of Figure 4. The histogram analysis for the GaN nanoparticles prepared with the matrix shows an average size of the nanoparticles of 20 nm, whereas for the GaN particles prepared without the matrix the histogram indicates the formation of larger size particles with multiple distributions. Moreover, the AFM images of the Mg^{2+}-doped GaN nanoparticles prepared without the matrix indicate the formation of larger aggregates (ca. 200 nm in size). These results highlight the importance of the La$_2$O$_3$ matrix in avoiding the sintering of Mg^{2+}-doped GaN nanoparticles to a greater extent during high-temperature nitridation. Though this matrix method avoids sintering of nanoparticles into larger clusters, sintering of 2 to 3 nanoparticles is inevitable as the void sizes between the La$_2$O$_3$ matrix particles are larger than the average size of Ga$_2$MgO$_4$ nanoparticles. This is clear from the increase in the average nanoparticle size to 20 nm after nitridation of the 8 nm precursor Ga$_2$MgO$_4$ nanoparticles (see Figure S1). We would like to emphasize that this method is easily optimized in the following ways: i) by increasing the mass ratio of La$_2$O$_3$ matrix to precursor oxide nanoparticles, ii) by matching the void sizes formed between the La$_2$O$_3$ particles to the size of the precursor particles, and iii) by developing co-precipitation methods where the precursor nanoparticles are prepared during the synthesis of the matrix materials.

3. Conclusions

Mg^{2+}-doped GaN nanoparticles were prepared by a simple solid-state reaction of Ga$_2$MgO$_4$ and NH$_3$ at 950°C. We utilized an inert matrix, namely, Eu^{3+}-doped La$_2$O$_3$, to suppress sintering of nanoparticles during this high-temperature nitridation. The Mg^{2+}-doped GaN nanoparticles exhibit bright blue-light emission near 410 nm and a weak yellow emission around 580 nm. The optical characteristics of the nanoparticles are not affected by the matrix. This method has the advantage that crystalline GaN nanoparticles can be synthesized without much sintering. Coating of GaN nanoparticles with TOPO leads to a good dispersibility in organic solvents such as ethanol.

4. Experimental Section

Materials: Ga(NO$_3$)$_3$·xH$_2$O, Mg(NO$_3$)$_2$·6H$_2$O, La(NO$_3$)$_3$·6H$_2$O, Eu(NO$_3$)$_3$·5H$_2$O, glycine, and trioctylphosphine (90%) were purchased from Aldrich and used as received. Aqueous ammonium hydroxide (28–30%) was purchased from Merck. Anhydrous ammonia gas (99.999%) used for the nitridation was purchased from Praxair. Milli-Q water with a resistance greater than 18 MΩ was used in all our experiments.

Preparation of Ga$_2$MgO$_4$ nanoparticles: Ga$_2$MgO$_4$ nanoparticles were prepared by the glycine-nitrate combustion method.[25,26] Stoichiometric amounts of Ga(NO$_3$)$_3$·xH$_2$O (1.25 mmol, assuming $x=8$), Mg(NO$_3$)$_2$·6H$_2$O (0.20 mmol), and glycine were dissolved in 25 mL of water by keeping a glycine-to-metal ion ratio of 1:2. The solution was slowly evaporated at 120°C, until a transparent residue was obtained. This was then heated to 220°C. The combustion reaction took place and a brownish-yellow-colored product was obtained. The resulting solid was then heated in flowing air at 650°C for 5 h to yield white Ga$_2$MgO$_4$ nanoparticles.

Preparation of Eu^{3+}(5%)-doped La$_2$O$_3$ powder: An aqueous solution was prepared by dissolving corresponding amounts of La(NO$_3$)$_3$·6H$_2$O and Eu(NO$_3$)$_3$·5H$_2$O. This solution was added dropwise to a flask containing 10 mL of 28% NH$_4$OH solution. The precipitate was washed well with Milli-Q water and dried in vacuum and then converted to Eu^{3+}-doped La$_2$O$_3$ by heating in air at 950°C for 12 h.

Preparation of Mg^{2+}-doped GaN nanoparticles: In a typical experiment, nanoparticles of Ga$_2$MgO$_4$ were mixed with Eu^{3+}-doped La$_2$O$_3$ powder in the ratio 1:10 (w/w) and ground well for proper mixing. This oxide mixture was placed in a quartz crucible that was put inside a quartz furnace. The nitridation was performed in an ammonia atmosphere. The temperature of the furnace was increased to 950°C at a rate of 5°C min^{-1}. This temperature was maintained for 3 h before it was cooled to RT at the same rate in the NH$_3$ atmosphere. The NH$_3$ flow was maintained at 10 sccm (standard cubic centimeter per minute). The resultant light-yellowish-white product was etched in a 10% HNO$_3$ solution for 1 h to remove all the La$_2$O$_3$ and MgO. The residue was washed with water and methanol, followed by drying under vacuum. The yield of GaN particles was essentially quantitative.

Coating of the Mg^{2+}-doped GaN nanoparticles with TOPO: The dried Mg^{2+}-doped GaN nanoparticles (15 mg) were mixed with 1.50 g of TOPO and refluxed for 24 h at 220°C in an argon atmosphere. The resulting solid was washed well with methanol to remove any uncoordinated TOPO. The nanoparticles were finally dispersed in absolute ethanol.

X-ray powder diffraction: Approximately 40–50 mg of the sample was gently stirred in an alumina mortar to break up all lumps. The powder was smeared on to a zero-diffraction quartz plate using ethanol. Step-scan X-ray powder-diffraction data were collected over the 2θ range 3–100° with CuKα (40 kV, 40 mA) radiation on a Siemens D5000 Bragg-Brentano θ–2θ diffractometer equipped with a diffracted-beam graphite monochromator crystal, 2-mm (1°) divergence and anti-scatter slits, 0.6-mm receiving slit, and incident beam Soller slit. The scanning step size was 0.04° 2θ with a counting time of 2 s per step.

AFM measurements: AFM images were recorded in the contact mode using a Thermo microscope AFM scanner having a silicon nitride tip (model MLCT-EXMT-A) supplied by Veeco Instruments. The nanoparticles were dispersed in absolute ethanol and sonicated for an hour before depositing on a thin glass plate (5 mm × 5 mm) by placing a drop of the dispersion followed by slow drying in air for approximately 1 h to avoid the capillary interactions during the drying process. The measurements were done with a resolution of 500 × 500 pixels per image and an image dimension of 50 μm × 50 μm. For the histogram analysis only particles that are smaller than 100 nm were taken into account. The reported values are based on the heights of the AFM features.

Photoluminescence (PL) measurements: Room-temperature PL measurements on the Mg^{2+}-doped GaN samples were performed using a 325-nm Omnichrome Series 74 He–Cd laser by Melles Griot. The laser beam was focused on the Mg^{2+}-doped GaN particles through the microscope. A SpectroPro-500 monochromator by Acton Research Corporation was used to scan the PL signal in the visible range (350–700 nm). The signal was amplified by a differential preamplifier and then acquired by the computer. The PL studies of the Eu^{3+}-doped La$_2$O$_3$ samples were carried out using an Edinburgh Instruments' FLS 920 with a 450 W Xe arc lamp and a red-sensitive Peltier-element-cooled Hamamatsu R928P PMT and making use of a solid sample holder. A KBr pellet was prepared by mixing the sample and KBr in a ratio of 1:10 and placed in a solid sample holder. The emission from the sample was collected from the reverse side of the pellet at an angle of 30° with respect to the source and normal to the sample surface. All spectra were recorded with 1 nm resolution and corrected for the instrument response.

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Supplementary Materials

Mg^{2+}-Doped GaN Nanoparticles as Blue emitters; a method to avoid sintering at

high temperatures

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[#] Both contributed equally to the work.
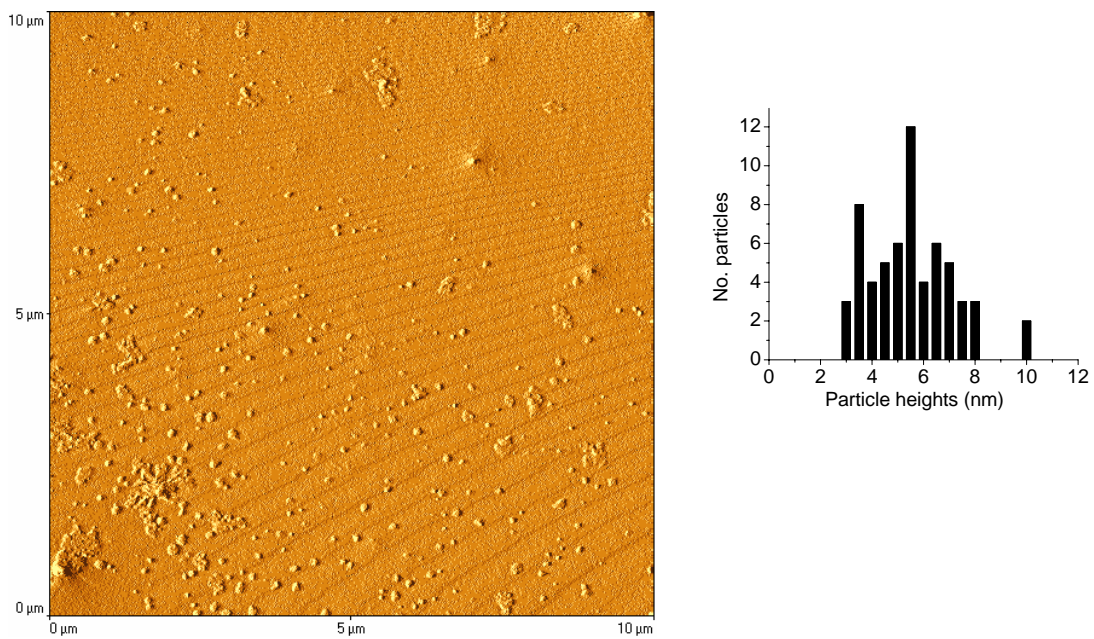
Figure S1. AFM image of the Ga_2MgO_4 nanoparticles prepared by glycine nitrate combustion method and dispersed in water.
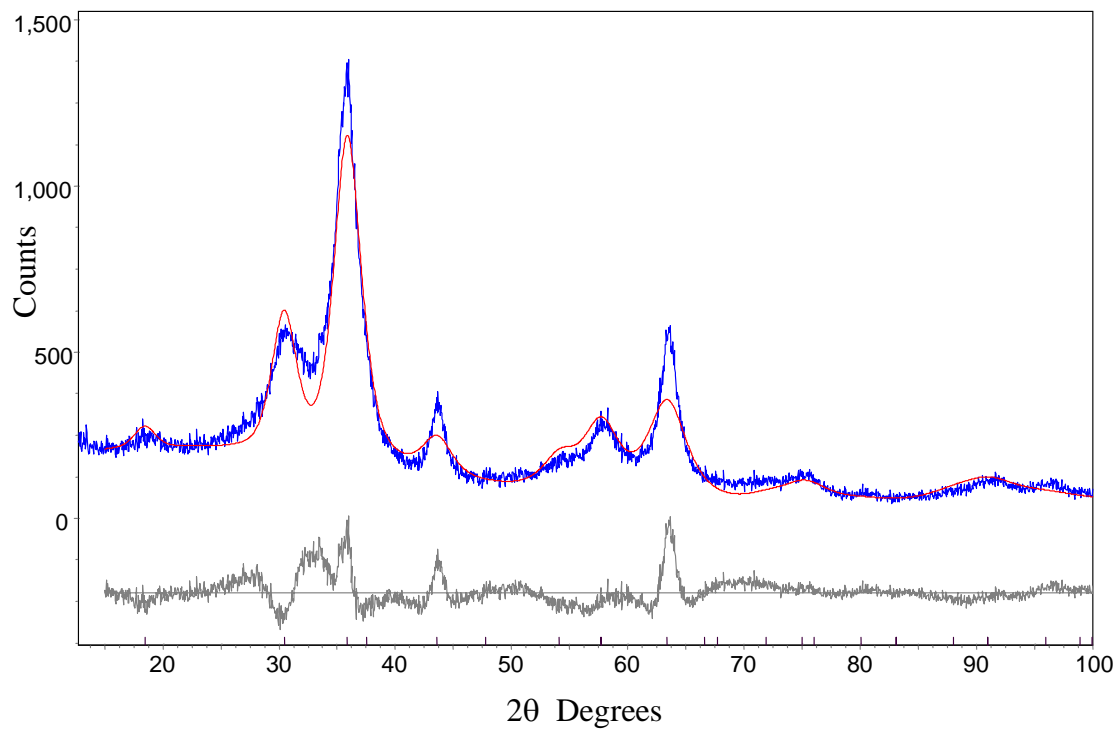
Figure S2. Experimental and calculated XRD pattern of Ga_2MgO_4 nanoparticles prepared by the combustion method. Tick marks below show the positions of X-ray diffraction peaks of Ga_2MgO_4. Grey line is the difference pattern (experimental minus calculated).
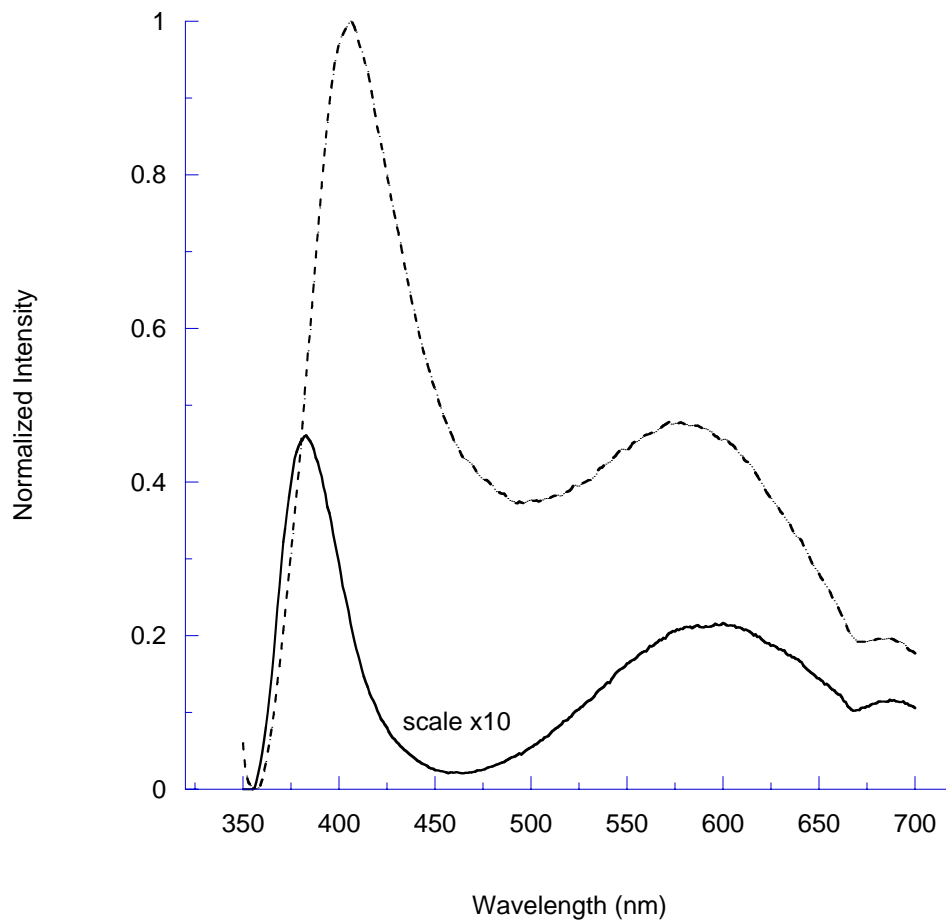
Figure S3. Emission spectra of GaN (solid trace) and Mg^{2+}-doped GaN nanoparticles (dottod trace).
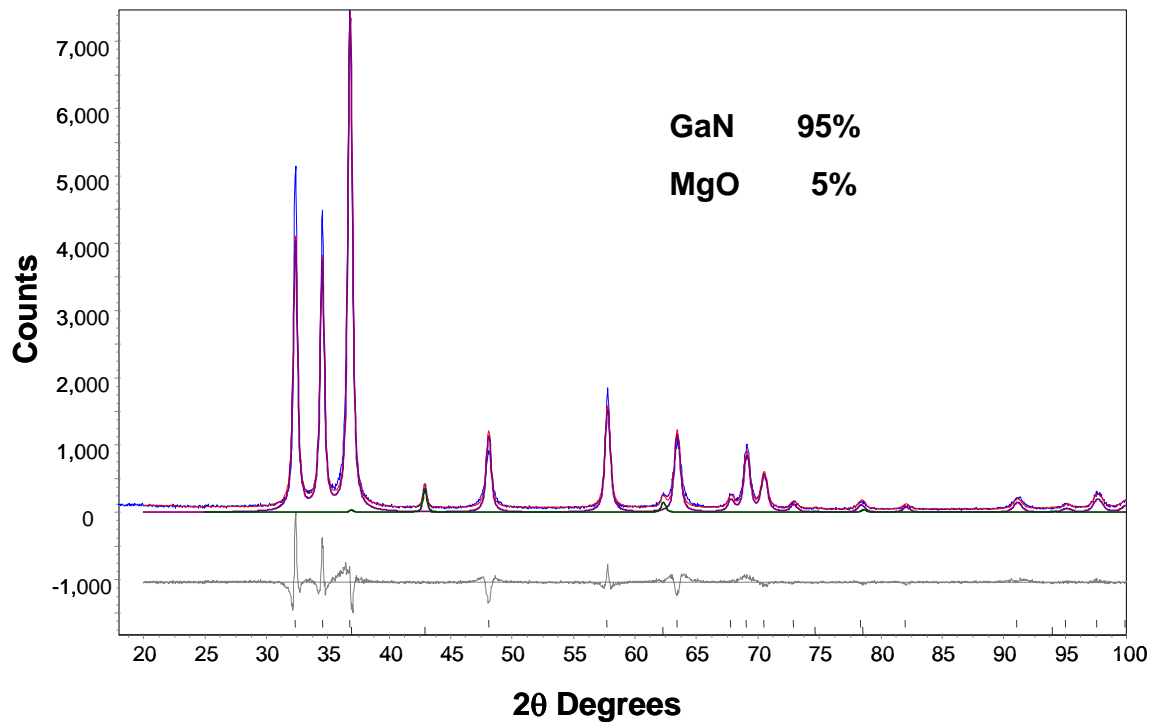
Figure S4. Experimental (blue) and calculated (red) XRD patterns of Mg^{2+}-doped GaN nanoparticles prepared without the matrix. Grey line is the difference pattern (experimental minus calculated). Tick marks below show the positions of X-ray diffraction peaks of GaN (purple) and MgO (green).
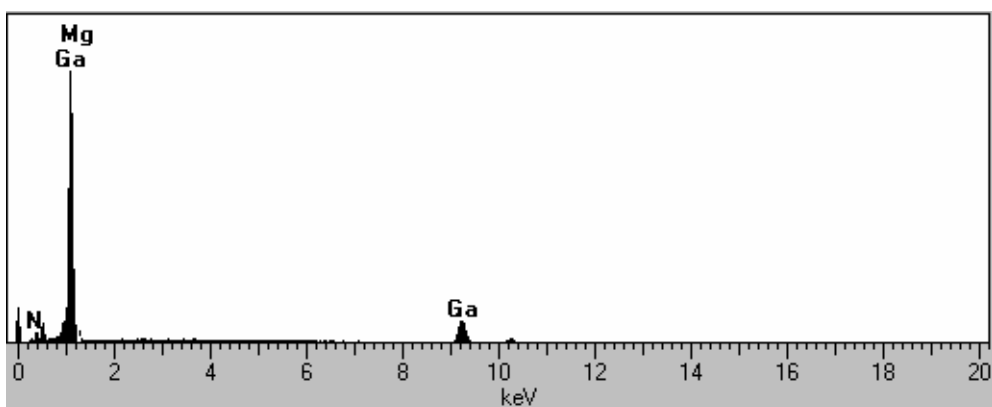
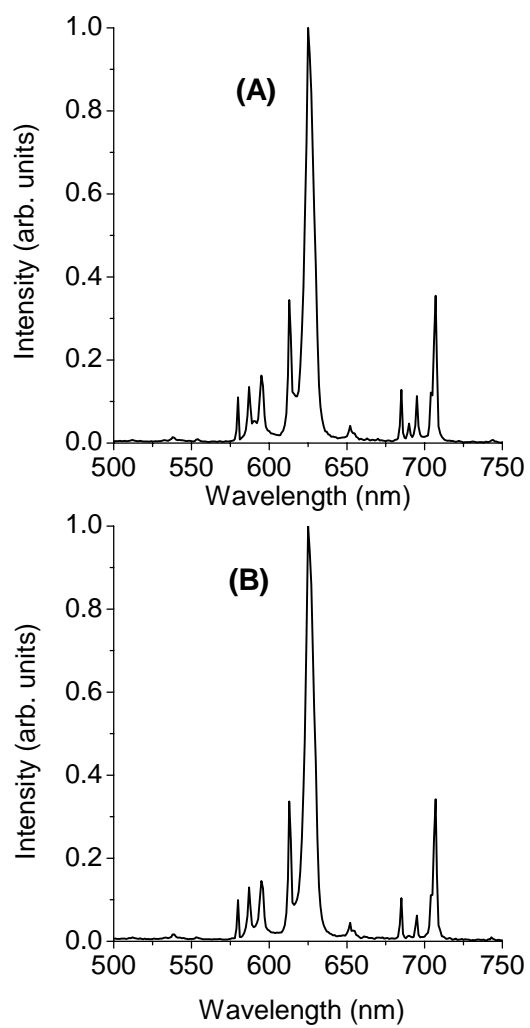**Figure S5.** EDS spectrum of Mg^{2+}-doped GaN nanoparticles after removal of the La_2O_3 matrix.

Figure S6. Emission spectra of Eu^{3+}-doped La$_2$O$_3$ particles (A) before and (B) after heating in NH$_3$ at 950 °C.
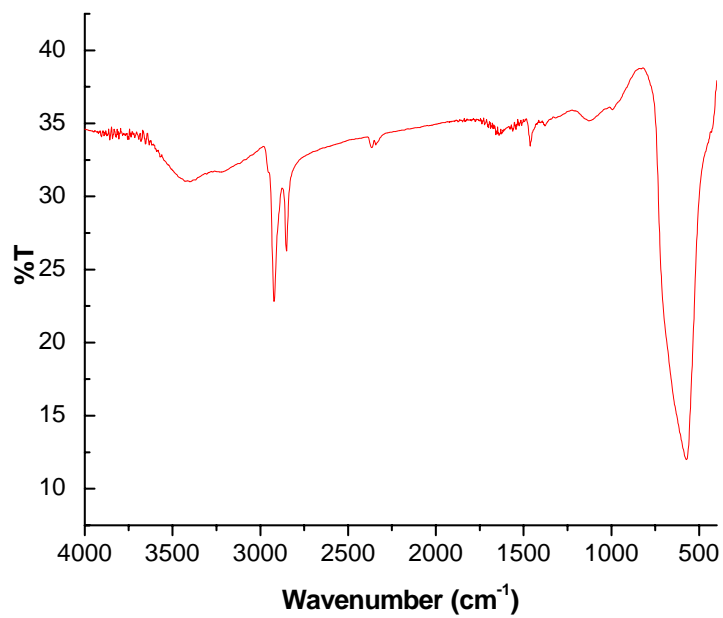
Figure S7. FTIR spectrum of TOPO coated Mg^{2+}-doped GaN nanoparticles.