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Preparation and characterization of Ga_2O_3 and GaN nanoparticles

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ABSTRACT

In this communication, we present results on preparation of GaN nanoparticles by conversion of Ga_2O_3 nanocrystals in a flow of NH_3 and H_2. The monoclinic Ga_2O_3 nanoparticles have been prepared by hydrothermal method with gallium nitrate and sodium hydroxide as precursors. Ga_2O_3 nanowires are produced with increasing the duration of the hydrothermal process up to 24 hours. The production of β-phase Ga_2O_3 has been confirmed by X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy. According to XRD, Raman and FTIR spectra, wurtzite type GaN nanocrystals with an average size of 28.6 nm are obtained by nitridation of Ga_2O_3 nanoparticles. Doping of Ga_2O_3 nanomaterial with Eu^{3+} ions in the hydrothermal process is demonstrated, and the emission spectra of this Eu-doped nanomaterial are compared with those of Eu-doped nanoparticles prepared previously by solid state reactions.

Ga_2O_3 nanoparticles; GaN nanocrystals; hydrothermal method; XRD spectroscopy, FTIR spectroscopy, Raman spectroscopy, photoluminescence

1. INTRODUCTION

The interest to preparation of nanoparticles on the basis of semiconductor and oxide materials comes from the influence of nanoparticle dimensionality upon their optical, radiative, and magnetic properties. Particularly, optical properties of GaN nanostructures are interesting for applications in solid-state lightening.[1,2] GaN materials can be synthesized by means of different methods, for instance by combustion in a NH_3 flow to convert the Ga_2O_3 nanoparticles to GaN ones.[3] GaN nanoparticles with sizes between 10 and 20 nm are obtained by this method. Monoclinic β-Ga_2O_3 nanoparticles have been obtained from $Ga(NO_3)_3$ dissolved in nitric acid by adjusting the pH of the solution through the addition of ammonium hydroxide with a subsequent thermal treatment of the produced GaO(OH) at the temperature of 400°C during 4 hours,[4] and a further thermal treatment of the Ga_2O_3 powder in a NH_3 flow at the temperature of 900°C during 10 to 120 minutes to produce GaN nanoparticles. A direct method of GaN nanoparticles synthesis from LiN_3 and $GaCl_3$ was also applied.[5,6] Good quality GaN nanocrystals have also been prepared by a simple and cost-effective sol-gel method with Ga_2O_3 powder, a mixture of concentrated HCl and HNO_3, citric acid, acetone, ammonium hydroxide, ethylenediamine, and free ammonia crude materials.[7]

In this paper, monoclinic Ga_2O_3 nanoparticles have been prepared by hydrothermal method with gallium nitrate as a source material. GaN nanoparticles have been produced by conversion of Ga_2O_3 in a flow of NH_3 and H_2. The XRD measurements demonstrate that the nanoparticle crystallinity depends upon the duration of thermal treatment, and upon the temperature of treatment in the NH_3 and H_2 flow. The high crystal quality has been confirmed by the presence of sharp and narrow peaks in the XRD spectrum.

2. RESULTS AND DISCUSSIONS

High purity $Ga(NO_3)_3$ $9H_2O$ and 1M NaOH chemicals from Sigma-Aldrich have been used for synthesis. The experimental procedure consists in dissolution of 2.5M of gallium nitrate in 50 ml of distilled water and adjustment of

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the solution pH to the value of 9 by means of the 1M NaOH solution under vigorous stirring. The suspension is introduced in a teflon autoclave with a steel shell to ensure a good sealing. The process lasts for 5 hours at the temperature of 220°C. The particle separation after autoclaving was performed by settling and filtering with a subsequent drying in an oven during 2 hours at 80°C. The scanning electron microscope (SEM) image of the powder produced with a 5 hours hydrothermal process is shown in Fig. 1a. With increasing of the duration of the hydrothermal process from 5 hours to 24 hours, Ga_2O_3 nanowires are produced with the morphology illustrated in Fig. 1b.

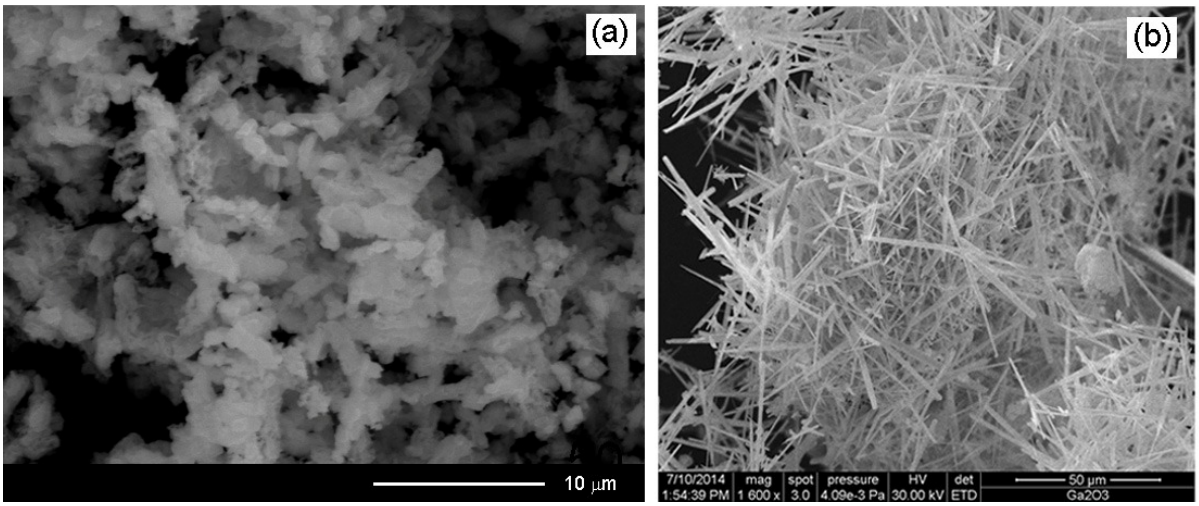


Figure 1. SEM image of the powder produced with 5 hours (a) and 24 hours (b) hydrothermal process.

The obtained powder was studies by means of XRD spectroscopy which demonstrated the presence of a single β - Ga_2O_3 phase (Fig. 2).

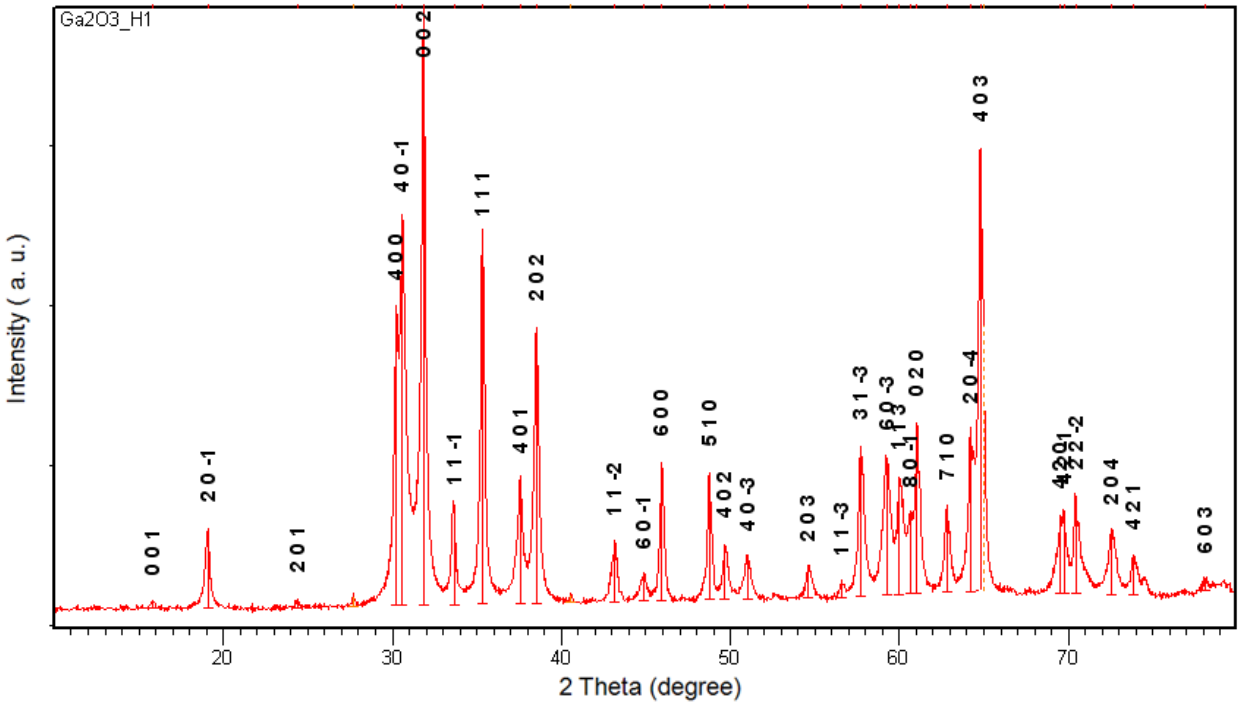


Figure 2. XRD pattern of Ga_2O_3 nanoparticle obtaining by hydrothermal method.

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Fourier transform infrared (FTIR) spectra also demonstrated the formation of β-Ga_2O_3 nanoparticles (Fig. 3, curve 1). The spectrum is dominated by the absorption bands at 455 cm^{-1} and 684 cm^{-1} which have been previously assigned to vibration modes of the Ga-O bonds in the β-Ga_2O_3 structure (A_u modes).[8] Other peaks observed at 528 cm^{-1}, 624 cm^{-1}, 748 cm^{-1} are related to B_u modes.

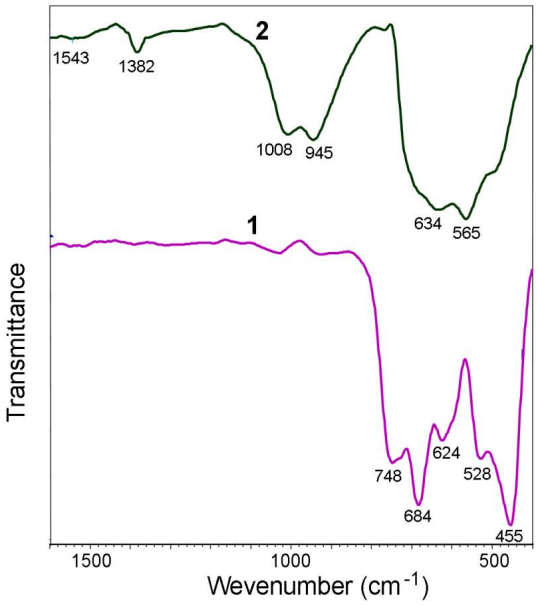


Figure 3. FTIR spectra of Ga_2O_3 nanoparticle obtaining by hydrothermal method (curve 1) and GaN nanoparticles produced from Ga_2O_3 nanoparticle (curve 2).

Good quality GaN nanoparticles have been produced from Ga_2O_3 nanocrystals under flowing ammonia with a subsequent nitridation in a mixture of NH_3 and H_2 with flow rates of 0.35 and 2.5 l/min, respectively. The Ga_2O_3 powder was placed into a horizontal tube furnace with a quartz boat and heated at temperature of 900-950 ^oC during 90-150 min After annealing, the furnace was switched off, and cooling down occurred in a natural fashion.

The diffraction peaks observed in the XRD pattern of the produced GaN powder can be indexed to a hexagonal wurtzite structure (Fig. 4). The sizes of the produced high crystallinity GaN nanoparticles deduced from the XRD spectra according to Sherrer formula are around 28.6 nm.

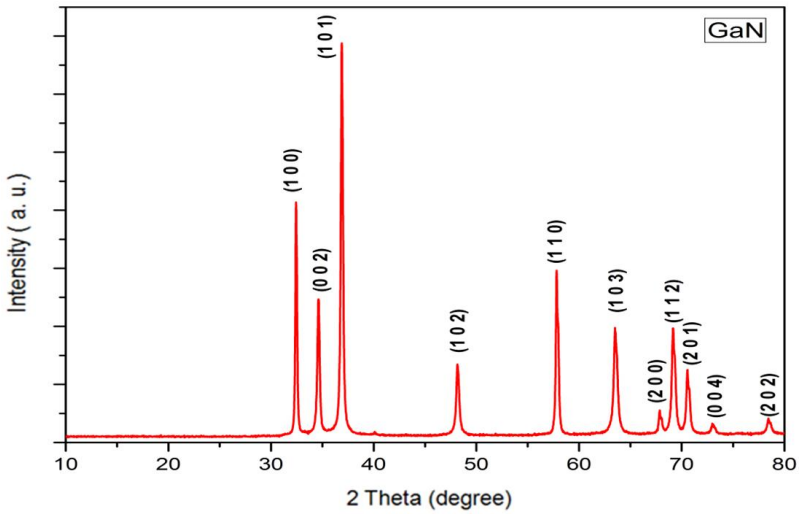


Figure 4. XRD pattern of GaN nanoparticle produced by annealing of Ga_2O_3 powder in a flow of NH_3 and H_2 during 120 min.

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This powder was also characterized by means of Raman scattering and FTIR spectroscopy. The Raman spectrum (Fig. 5) measured in the wavenumber range from 300 to 800 cm^{-1} shown the presence of peaks at 534 cm^{-1}, 561 cm^{-1} and 569 cm^{-1} assigned to $A_1(TO)$, $E_1(TO)$, and E_2-high vibration modes, respectively, as well as a weak band at 730-740 cm^{-1} assigned to the $A_1(LO)$ and $E_1(LO)$ modes. The low intensity of the LO modes is likely due to the presence of a high free carrier concentration in the nanoparticles. A Raman scattering band was also observed at 420 cm^{-1}, which has been previously assigned to an acoustic overtone.[9]

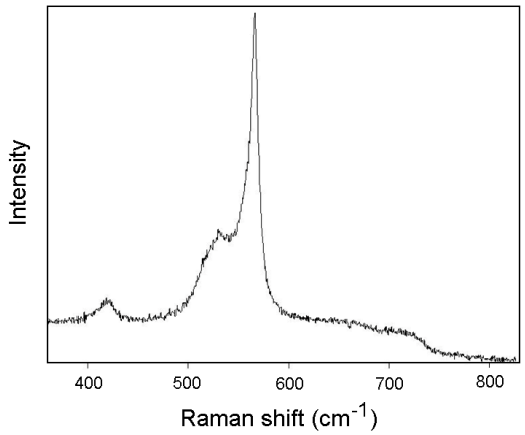


Figure 5. Raman spectrum of GaN nanoparticle produced by annealing of Ga_2O_3 powder in a flow of NH_3 and H_2 during 120 min.

No absorption bands related to the Ga_2O_3 phase are observed in the FTIR spectra of the prepared GaN nanoparticles (Fig. 3, curve 2). The spectrum is dominated instead by two absorption bands at 565 cm^{-1} and 634 cm^{-1}. The first one has been previously attributed to the Ga–N stretching vibration ($E_1(TO)$ mode) in the hexagonal type GaN crystals,[10] while the second one is related to a local vibration mode (LVM) attributed to nitrogen and gallium vacancies.

In order to dope the Ga_2O_3 nanopowder with Eu^{3+} ions, $EuCl_3$ with concentration from 0.3 to 3 at% was added to the 0.05M $Ga(NO_3)_3$ solution which was subjected to stirring with a magnetic stirrer during 30 minutes. The pH of the solution was adjusted to 9.5 by means of 25% NH_4OH under additional stirring for 30 minutes. The obtained suspension was introduced in a teflon autoclave with a steel shell for thermal treatment as described above. The incorporation of the Eu^{3+} ions into the powder was investigated by means of photoluminescence (PL) spectroscopy. The PL spectra were excited by the 405 nm line of a mercury lamp at room temperature. The PL spectrum of a sample doped with a 2% concentration of Eu is shown in Fig. 6.

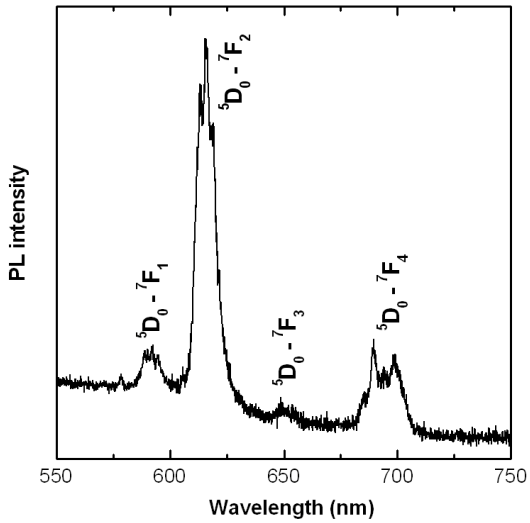


Figure 6. PL spectrum of Ga_2O_3 nanoparticle doped with Eu^{3+} ions obtaining by hydrothermal method.

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All the observed lines are consistent with Eu^{3+}-related radiative electron transitions, namely with $^5D_0 \rightarrow {}^7F_j$ (J = 1,2,3,4) transitions. The structure of β-Ga_2O_3 is monoclinic with a space group of C2/m, and Ga^{3+} ions occupy either tetrahedral or octahedral crystallographic sites. With regular tetrahedrons and octahedrons, the local site symmetry of Eu^{3+} ions substituting Ga^{3+} ions would be T_d or O_h, respectively. However, the tetrahedrons and octahedrons are distorted in the real β-Ga_2O_3 structure, and the point-group of these sites should be lower than T_d and O_h. In fact, both these sites have the same site symmetry of C_s.[11] Since the ionic radii of the Ga^{3+} ions are 0.047 and 0.062 nm for tetrahedral and octahedral coordination, respectively,[12,13], taking into account the ionic radius of the Eu^{3+} ions (0.095 nm), the distorted octahedral site should be more suitable for Eu^{3+} ions. The incorporation of Eu^{3+}ions in this site symmetry was previously confirmed in Eu^{3+}-doped β-Ga_2O_3 nanophosphors annealed at 1100°C, where sharp and well-resolved transition lines were observed.[14] On the other hand, the spectrum presented in Fig. 6 is similar to that observed in a nanophosphor annealed at 900°C. [14] The fact that some sharp transition lines of Eu^{3+} ions emerge for the sample annealed at 900°C, was suggested to be an indication that a small portion of Eu^{3+} ions is incorporated into the crystal lattice, while the main signal comes from the Eu^{3+} ions that occupied a surface or near surface site of nanoparticles. As a result, the emission lines associated with crystal field levels of Eu^{3+} ions are poorly resolved due to the inhomogeneous broadening of the spectra.

Figure 7 compares the PL spectrum of the Eu^{3+} doped sample produced by hydrothermal method with the spectrum of a Ga_2O_3 powder phosphor produced previously by solid phase reaction method. One can see that, in contrast to the sample produced by hydrothermal method, the spectrum of the sample produce by solid phase reaction is characterized by broader superimposing lines usually observed in amorphous materials and glasses.

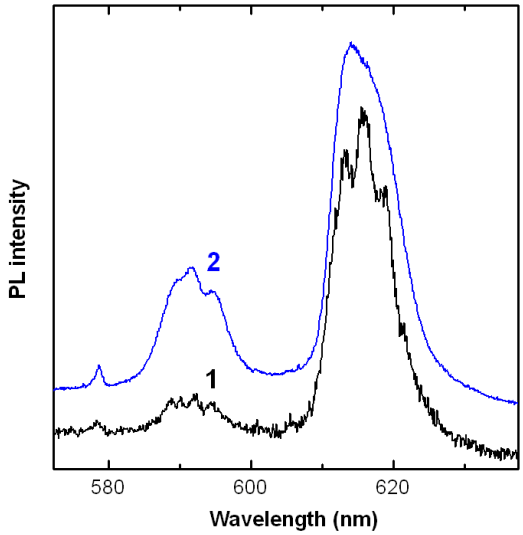


Figure 7. PL spectrum of Ga_2O_3 nanoparticles doped with Eu^{3+} ions obtaining by hydrothermal method (1) and solid phase reactions (2).

3. CONCLUSIONS

The results of this paper demonstrate preparation of monoclinic Ga_2O_3 nanoparticles and nanowires by hydrothermal method with gallium nitrate as a source material, and doping of this nanomaterial by Eu^{3+} ions, as well as obtaining of GaN nanoparticles by conversion of Ga_2O_3 in a flow of NH_3 and H_2. The SEM images demonstrate that the morphology of the produced nanomaterial depends upon the duration of the hydrothermal, while the XRD measurements demonstrate that the GaN nanoparticle crystallinity depends upon the duration of thermal treatment, and upon the temperature of treatment in the NH_3 and H_2 flow. The high crystal quality has been confirmed by the presence of sharp and narrow peaks in the XRD spectrum, as well as by Raman scattering and FTIR spectroscopy. The analysis of emission lines related to Eu^{3+} radiative electron transitions in the PL spectra of Ga_2O_3 nanoparticles prepared by hydrothermal method demonstrates their better crystallinity as compared to those prepared by solid phase reactions.

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