

Synthesis and Characterization of GaP Nanoparticles for Light Emissive Devices

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ABSTRACT

This work reviews our recent efforts to prepare high quality GaP nanoparticles. for use in light emissive nanocomposites as well as for comparison of their optical properties with GaP bulk crystals.

The nanoparticles have been prepared by colloidal low temperature methods using ultrasonic and ultracentrifuge treatment in order to improve the quality of nano-suspension and to characterize their dimensions. Trioctylphosphine oxide (TOPO) was used to prevent coagulation and aggregation of nanoparticles. Photoluminescence and Raman light scattering spectra were collected, X-ray diffraction and high resolution microscopy of the nanoparticles prepared under different conditions are compared with each other as well as with those from bulk single crystals.

We demonstrate that thorough ultrasonic treatment as well as use of an ultracentrifuge, a pure fraction of nanoparticles of about 10 nm in diameter result with a luminescence maximum up to 3.2 eV. Selected mixtures of GaP nanoparticles, based on dimensions, exhibit broad band luminescence from UV until yellow-red region with controlled width and position of maximum.

Keywords: GaP nanoparticles, colloidal synthesis, characterization

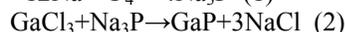
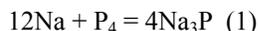
1 INTRODUCTION

In this work we review the continuation of efforts, initially discussed at the 2006 and 2010 Nanotech Conferences [1-3], with the focus being to advance the quality of GaP nanoparticles for light emissive devices by using different methods for their syntheses and polymers for the preparation of GaP based nanocomposites [1-8].

2 EXPERIMENTAL PROCEDURE AND DISCUSSION

In order to improve the quality of GaP nanocrystals of small dimensions with the pronounced quantum confinement effect, the colloidal method of syntheses of

GaP nanoparticles [9, 10] has been used instead of the hydrothermal method earlier [1, 2]. The nanoparticles were synthesized through the reaction between anhydrous gallium chloride (GaCl₃) and sodium phosphide (Na₃P). Na₃P was used in an Ar-filled glove-box through the reaction of white P and Na in toluene. The reaction went for 8 hrs. at 110°C, ultrasonication and mechanical mixing until completion of the process with creation of black suspension of Na₃P in toluene. For the syntheses of GaP nanoparticles 0.8 g of GaCl₃ were dissolved in 30 mL of anhydrous toluene and the solution mixed under heat at 100°C. Then 1.5 g of Na₃P was dissolved in 50 mL of toluene and added to the GaCl₃ solution which was reacted for 2 hrs at 100°C under mechanical mixing. Thus, GaP nanoparticles were obtained as the result of the reactions:



The capping agent - trioctylphosphine oxide (TOPO) was added to the reaction mixture to prevent coagulation of the GaP nanoparticles and as the result the particles with the 10-60 nm dimensions have been obtained.

Poly (2-vinylpyridine) (P2VP), biphenyl vinyl ether (BPVE) and tetrahydrofuran (THF) polymers were used for preparation on GaP nanocomposites. Thickness of the polymer composite film was within 250-300 nm as determined by Atomic Force Microscopy (AFM). Thermo gravimetric analysis (TGA) was used to evaluate the decomposition of the nanocomposites. The procedures used in fabrication of the nanocomposites are described in the paper [3]. Note, that the light emissive nanocomposites of the best quality can be obtained only from a suspension that is thoroughly washed, ultrasonicated and subsequently dried.

The dried powders of GaP nanoparticles and GaP nanocomposites were then characterized using standard methods of Raman light scattering (RLS), X-ray diffraction (XRD), scanning probe microscopy (SPM), and photoluminescence (PL). For comparison, an industrial and specially grown and aged GaP single crystal was used.

The instruments for Raman light scattering and luminescence included Spectrograph Triax 552 interfaced

to Symphony CCD detection system and Coherent Innova 100-3K Krypton Ion Laser System. The spectra of Raman scattering was obtained at room temperature by excitation with 752.5 nm radiations and calibrated with the relevant etalons.

X-ray diffraction data were collected on Rigaku ULTIMA IV powder diffractometer using a monochromator and Cu K α radiation (1.5406 Å). All scans were in the θ - θ mode at 300 K.

Scanning probe microscopy (SPM) studies were performed on a Dimension 3100 atomic force microscope (AFM) from Digital Instruments, Inc. Tapping mode was used to study the surface morphology of the films in ambient air. Silicon tips with spring constants of 50 N/m were used. Imaging was conducted at scan rates in the range 1 Hz.

Luminescence (PL) was excited by the N₂ laser nanosecond pulses at wavelength 337 nm and measured at room temperature.

Figure 1 shows the AFM/SPM topography images of the GaP/ P2VP nanocomposite prepared on the base of the

suspension of GaP/TOPO nanoparticles in anhydrous ethanol (the composition according to TGA was 15% GaP, 85% – the polymer). One can see the uniform structure of the GaP/polymer nanocomposite, having the particles of the necessary for the quantum confinement effect dimensions of (10-50) nm.

In **Figure 2** one can see spectra of Raman light scattering from perfect GaP bulk crystals (**spectrum 1**) and GaP nanoparticles prepared by the colloidal (**spectrum 2**) or mild aqueous syntheses (**spectrum 3**). In the figure the mostly characteristic region of transversal and longitudinal optic phonons (TO and LO respectively) is presented.

Note that according to the Raman light scattering the characteristic phonon lines from GaP bulk and nanocrystals are narrow and intense, but only the nanoparticles thoroughly prepared by colloidal syntheses in presence of the capping agent TOPO demonstrate absolutely the same as in the bulk perfect crystals energy of the LO phonons, while they were weak, broad and shifted in the case of any nanoparticles prepared by the other method [1, 2] or under non-ideal conditions.

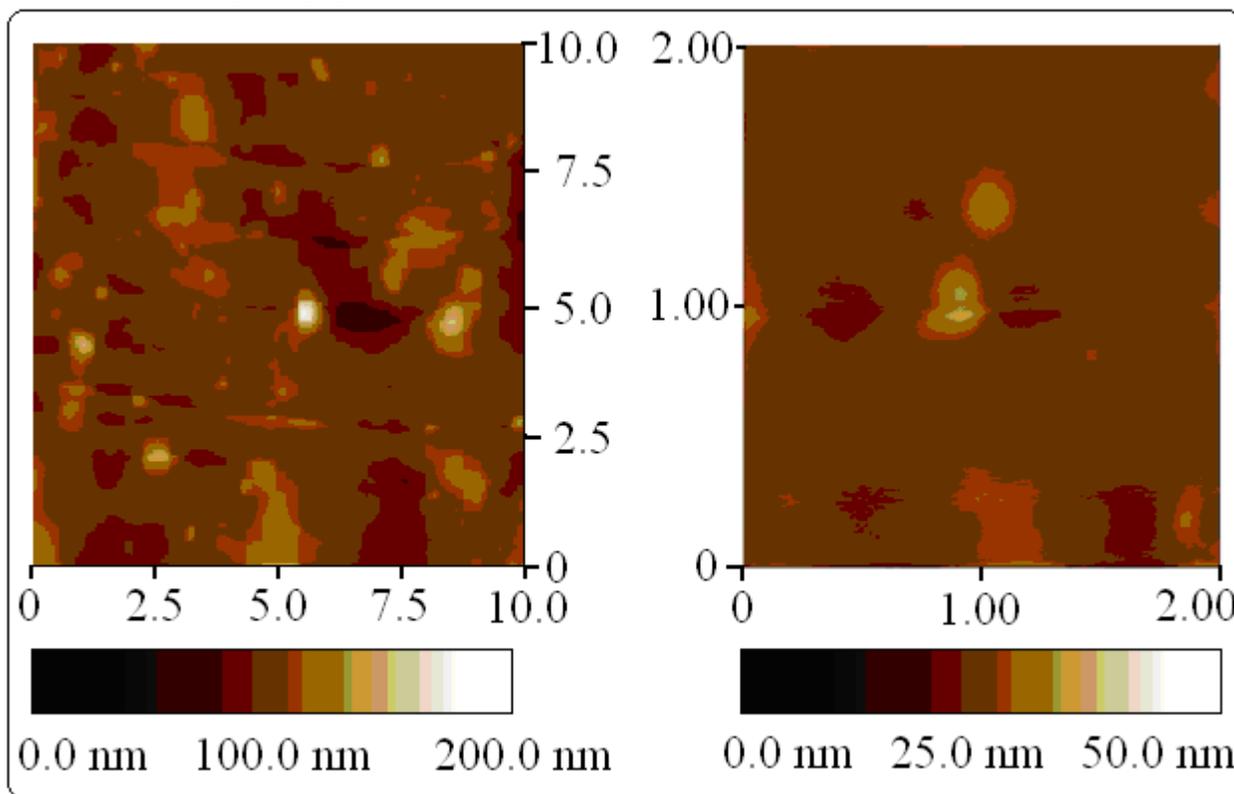


Figure 1: AFM/SPM topography images of the GaP/ P2VP nanocomposite prepared on the base of the suspension of GaP/TOPO nanoparticles in anhydrous ethanol.

In **Figure 3** one can see X-ray diffraction from GaP/TOPO nanoparticles prepared by the colloidal syntheses under the ideal conditions (**spectrum 1**) in comparison with the diffraction from perfect GaP single crystal (**spectrum 2**) as well as the XRD characteristic lines at 28.4 degree dependently on the average dimensions of the nanoparticles in a GaP/polymer nanocomposite

(**spectra 3** and **4**). Evaluation of average dimensions of the nanoparticles according to the Scherrer equation yields about 50 and 70 nm for the **spectra 3** and **4** respectively. These nanoparticles obtained by the colloidal synthesis also as the best samples of hydrothermal synthesis [1, 2] develop clear and narrow characteristic lines like those obtained from perfect GaP bulk single crystals taken from our unique

collection [4-8] of long-term (app. 50 years) ordered GaP single crystals (**Fig. 3, spectra 1 and 2**). It is important to note that slightly changing the conditions of the colloidal synthesis can change the average dimensions of the nanoparticles and, as the consequence, the spectral characteristic of luminescence.

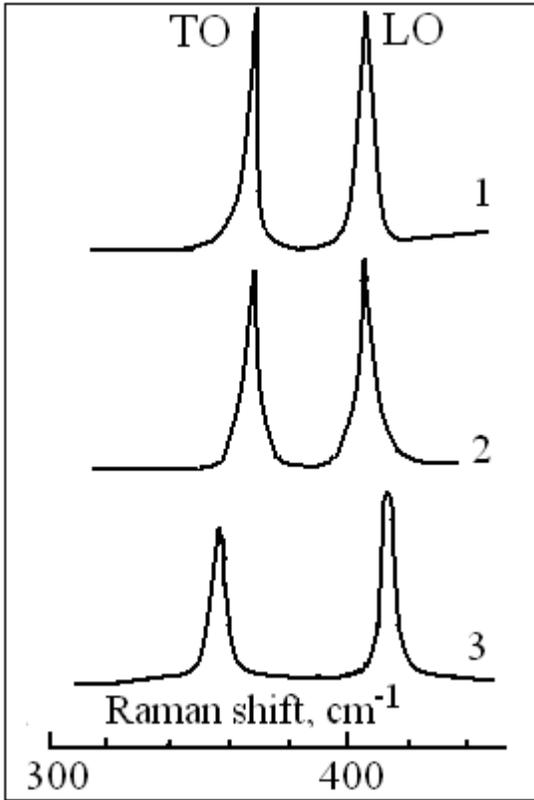


Figure 2: Raman light scattering from perfect GaP bulk crystals (**spectrum 1**) and GaP nanoparticles prepared by the colloidal (**spectrum 2**) or mild aqueous syntheses (**spectrum 3**).

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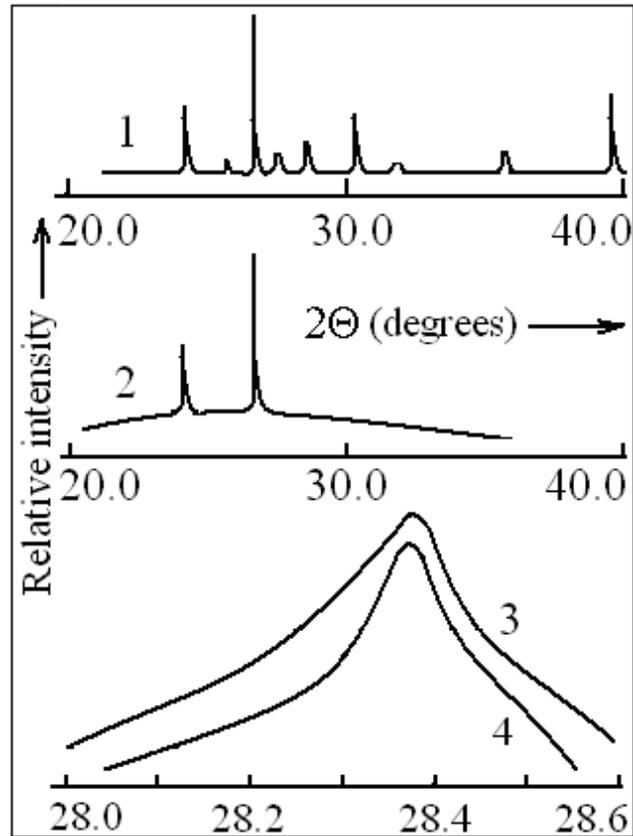


Figure 3: X-ray diffraction from GaP/TOPO nanoparticles (**spectrum 1**) in comparison with the diffraction from perfect GaP single crystal (**spectrum 2**) and in the dependence on their average dimensions (**spectra 3 and 4**)

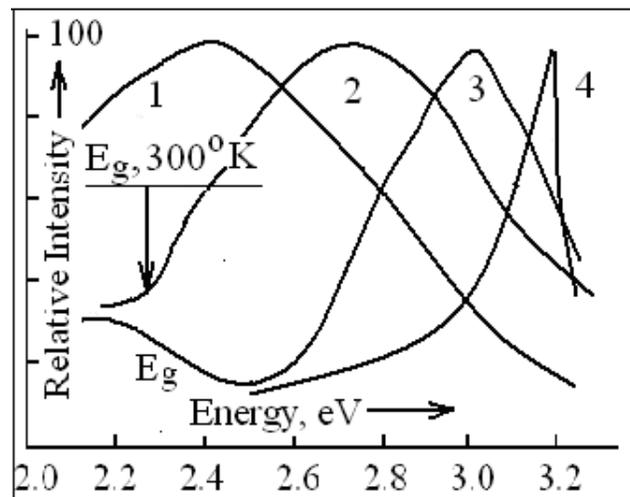


Figure 4: Luminescence of GaP nanoparticles prepared at different conditions (spectra 2-4) and in comparison with the luminescence of perfect GaP bulk single crystals (1).

REFERENCES

Figure 4 presents luminescence spectra of long-term (up to 50 years) ordered GaP single crystals (**spectrum 1**) in comparison with the spectra of GaP nanoparticles (and their nanocomposites), prepared under different conditions. As already noted, luminescence was absent at room temperature in newly-grown bulk single crystals, but the same crystals, aged app. 50 years, exhibit bright broad band luminescence at 300°K between 1.8 – 3.2 eV with the maximum blue-shifted from the position of the GaP forbidden gap ($E_g = 2.24$ eV).

Nearly the same spectrum of luminescence is observed from nanocrystals provided that they are not separated on their dimension (**spectrum 2**). The nanocrystals stored as dry powder demonstrate rather broad luminescent band with maximum at 3 eV (**spectrum 3**). At last, GaP/TOPO nanocrystals, thoroughly separated and distributed in a suspension, that prevent their coagulation, mechanical and optical interaction, have bright narrow-band luminescence with maximum at 3.2 eV, app. 1 eV far from the position of the absorption edge in GaP at 300°K (**spectrum 4**).

3 CONCLUSIONS

Nanoparticles of GaP have been prepared by colloidal low temperature synthesis. The spectra of PL, RLS, and XRD together with AFM/SPM images of the nanoparticles prepared under different conditions have been compared with each other as well as with those from perfect bulk single crystals. Uniform GaP nanoparticles, after ultrasonic treatment and a number of other operations, improved in quality and nanoparticles exhibited a broad band bright luminescence at room temperature with the maximum at 3 – 3.2 eV.

Polymer nanocomposites prepared from these nanoparticles will be reported separately.

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