# Preparation and Characterization of Nanocrystalline GaP for Advanced Light Emissive Device Structures

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## ABSTRACT

Presented here are recent efforts to enhance the quality of GaP nanoparticles for light emissive devices. GaP nanoparticles have been prepared by mild aqueous synthesis methods and their properties characterized by photoluminescence (PL), Raman light scattering (RLS), x-ray diffraction (XRD) and transmission electron microscopy (TEM). Due to pronounced quantum confinement effects the optical properties of GaP nanoparticles are considerably different from those of bulk crystals or particles whose dimensions exceed that of the Bohr exciton (app. 10nm). In this work, uniform GaP nanoparticles with bright luminescence at room temperature in a broad band with maximum at 3 eV have been obtained using yellow phosphorus, low temperature synthesis, and ultrasonic treatment that are found to improve the quality of the nano-suspension. The results of the nanoparticles characterization by the above mentioned methods clearly testify their high quality.

***Keywords***: GaP nanoparticles, mild aqueous synthesis

## 1 INTRODUCTION

This work reviews our recent efforts to advance the quality of GaP nanoparticles for light emissive devices based on polymer/GaP nanocomposites.

The choice of materials is based on their complementary behavior since each is a candidate for use in light emitters, waveguides, converters, accumulators and other planar, fiber or discrete micro-optic elements. While bulk and thin film GaP has been successfully commercialized for many years, its application in nanocomposites as a new optical medium has only received attention recently.

The fabrication and properties of the GaP/polymer nanocomposites for advanced light emissive device structures is discussed in another talk presented at the 2010 Nanotech Conference [1].

These papers presented to the 2010 Nanotech Conference have been fulfilled in framework of the STCU (www.stcu.int) 4610 Project "Light Emissive Device Structures" and are a part of the US/Moldova Program on advanced light-emissive sources on the base of transparent robust fluoropolymer and GaP nanoparticles [2-10].

## 2 EXPERIMENTAL PROCEDURE AND DISCUSSION

Nanoparticles of GaP have been prepared by mild aqueous synthesis [11-13] at different temperatures, modifications and compositions of the reacting components.

Noted here are only essential details of the aqueous syntheses as the base for comparison of nanoparticles prepared at different temperatures, modifications and compositions of the reacting components.

NaOH pellets were dissolved in distilled water. $Ga_2O_3$, red or yellow phosphorus powder and $I_2$ were mixed and added to the NaOH solution. The mixed solution was then placed into an autoclave and heated there in an oven for 8 hours at 200 or 125°C. After the completion of heating the autoclave was taken out of the oven and cooled. The obtained powder was filtered, washed with ethanol, and dried or ultrasonicated in the bath with a special solvent for separation in dimensions and preparation of a suspension for any nanocomposite. The dried powders were then characterized using standard methods of XRD, TEM, Raman scattering and photoluminescence. For comparison we used also industrial and specially grown and aged GaP single crystals [2-10].

The instruments for Raman light scattering and luminescence included spectrographs interfaced to a liquid nitrogen-cooled detector and an argon ion laser or lamp excitation sources. The spectra of Raman scattering was obtained at room temperature by excitation with 514.5 nm radiations and calibrated with the relevant etalons. Luminescence was excited by UV light of the lamps or the $N_2$ laser nanosecond pulses at wavelength 337 nm and measured at room temperature [9].

**Figure 1** shows the TEM images of GaP nanoparticles obtained by the aqueous synthesis. One can see GaP

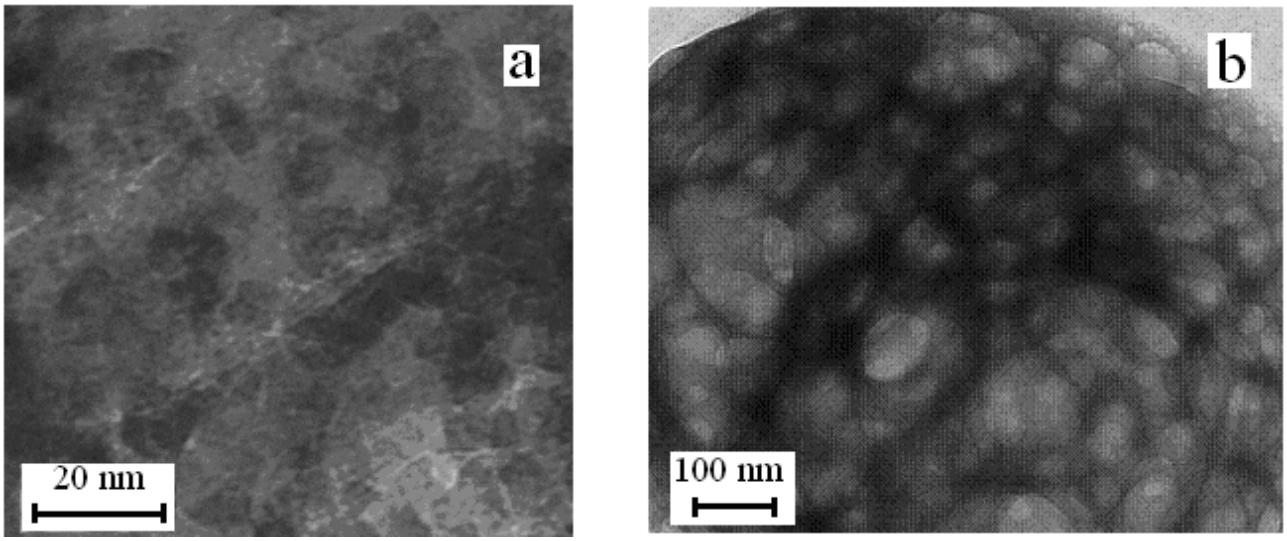


Figure 1: TEM images of GaP nanoparticles obtained by the aqueous synthesis. **a**. Thoroughly ultrasonicated and dried nanopowder. **b**. Initial clusters with the dimensions of the order of 100 nm.

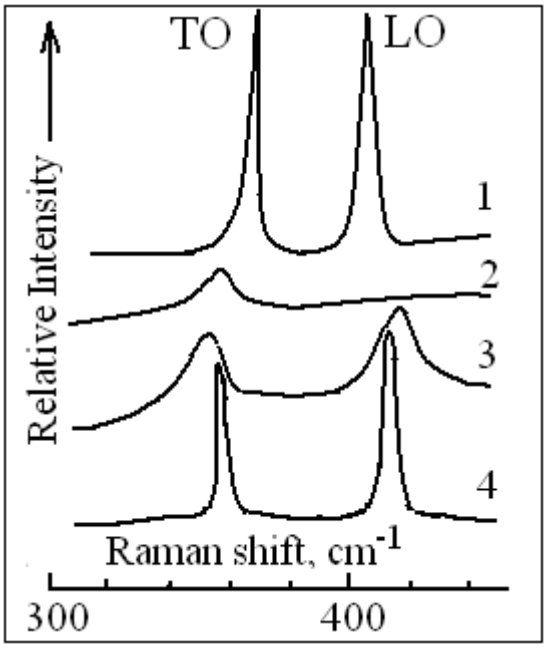


Figure 2: Raman light scattering from GaP nanoparticles of different treatment (spectra 2-4) and in comparison with perfect GaP bulk crystals (spectrum 1). 2. Not thoroughly treated powder of nanoparticles prepared using red phosphorus at 200°C. 3. Thoroughly treated GaP nanoparticles prepared using red phosphorus at 200°C. 4. Nanoparticles prepared on the base of yellow P by low temperature syntheses.

nanoparticles, having characteristic dimensions less than 10 nm. The washed, thoroughly ultrasonicated and dried nanopowder contains mainly single nanoparticles **(Fig. 1a)**, obtained from the initial clusters with the dimensions of the order of 100 nm **(Fig. 1b)**.

**Figure 2** shows spectra of Raman light scattering from GaP nanoparticles prepared on the base of yellow or red P by mild aqueous synthesis at increased or low temperatures and ultrasonically treated.

The characteristic GaP Raman lines from the doped aged GaP single crystals as well as from the nanoparticles prepared using yellow P by low temperature were narrow and intense **(Fig. 2, spectrum 1** and **4** respectively**)** whereas, they were weak and broad from the any nanoparticles prepared at high temperatures **(Fig. 2, spectra 2** and **3)**. The especially weak and broad spectrum exhibits not thoroughly washed powder (please see **spectrum 2**; spectra 1-3 are taken from [13]).

In **Figure 3** one can see X-ray diffraction from GaP nanoparticles prepared at different conditions using red or yellow phosphorus (**spectra 1-3**) in comparison with the diffraction from perfect GaP single crystal (**spectrum 4**). The nanoparticles obtained by low temperature aqueous synthesis using yellow phosphorus develop clear and narrow characteristic lines like those obtained from perfect GaP bulk single crystals taken from our unique collection of long-term (more than 40 years) ordered GaP single crystals (**Fig. 3, spectra 1** and **4**). Contrary to that, nanoparticles prepared on the base of red phosphorus or not in the best conditions show broad and weak characteristic lines (**Fig. 3, spectra 2** and **3).**

The luminescence was absent in newly-made industrial and our freshly prepared crystals but it was bright in the 40 years aged crystals (**Fig. 4, spectrum 1**; the features of luminescence in the perfect 40 years aged crystals please see in [3, 5, 7, 10]). Initial results on luminescent properties of GaP nanoparticles [13] confirm the preparation of 10 nm GaP nanoparticles with clear quantum confinement effects

but the luminescent spectrum was not bright enough and its maximum was only slightly shifted to UV side against the 2.24 eV forbidden gap at room temperature **(Fig. 4, spectrum 2)**. The nanoparticles obtained from the reaction with yellow P at low (125°C) temperature exhibit bright broad band spectra considerably shifted to UV side **(Fig. 4, spectrum 3, 4)**. Note that the original powder contains only a part of GaP particles with nearly 10 nm dimension, which develop quantum confinement effect and the relevant spectrum of luminescence, so the spectrum of luminescence consists of this band with maximum at 3 eV and of the band characterizing big particles with the maximum close to the edge of the forbidden gap in GaP **(Fig. 4, spectrum 3)**, but the thorough ultrasonic treatment gives an opportunity to get the pure fraction of nanoparticles with the **spectrum 4** having the maximum at 3 eV**.**

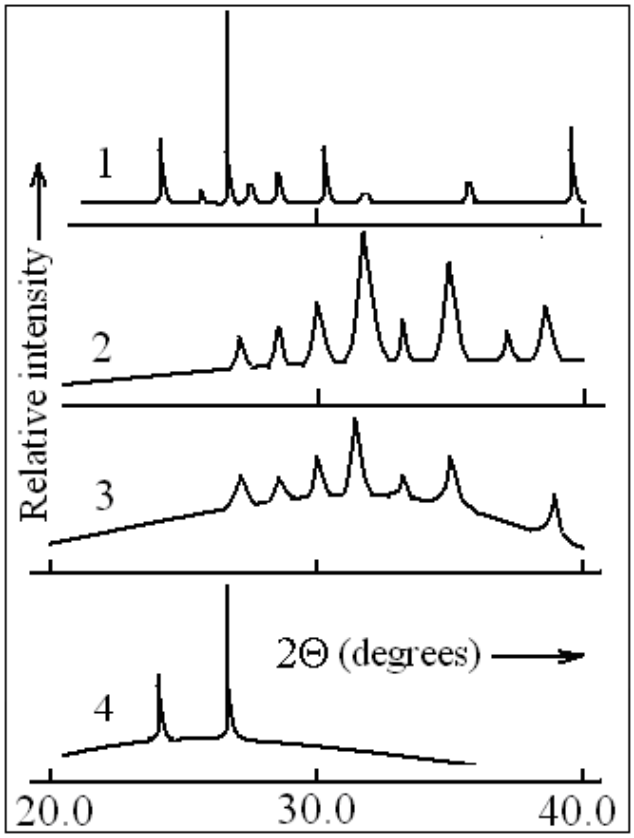


Figure 3 : X-ray diffraction from GaP nanoparticles. 1. Yellow phosphorus, best performance of low temperature syntheses, well-treated powder. 2. Yellow P, not the best performance and powder treatment. 3. Red phosphorus, the best result.

This work also continues monitoring of properties of GaP single crystals grown 40 years ago [2-10, 13]. We investigate their optical and mechanical properties in present in comparison with the data obtained in the 1960s, 1970s, 1980s and 1990s. Note that due to a significant number of defects and a highly intensive non-radiative recombination of non-equilibrium current carriers, initially luminescence of fresh undoped crystals could be observed only at the temperatures 80K and below. Now luminescence is clearly detected in the region from 2.0 eV and until 3.0 eV at room temperature (see **Figure 4**, **spectrum 1**). Taking into account that the indirect forbidden gap is only 2.25 eV, it is suggested that this considerable extension of the region of luminescence to the high energy side of the spectrum as well as a pronounced increase of its brightness are connected with a very small concentration of defects, considerable improvement of crystal lattice, high transparency of perfect crystals, low probability of phonon emission at rather high temperature and participation of direct band-to-band electron transitions.

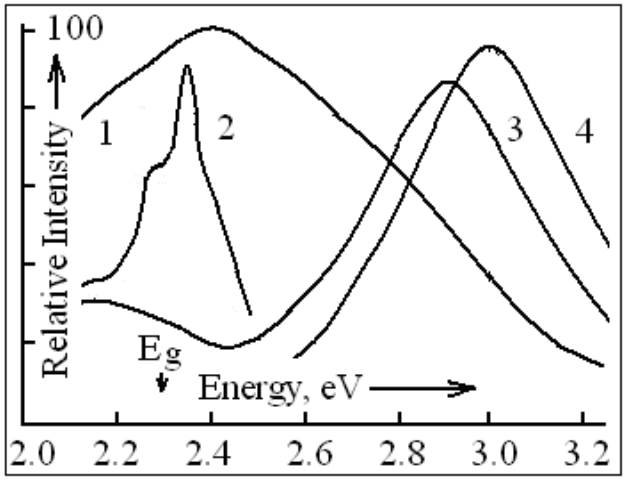


Figure 4 : Luminescence of GaP nanoparticles prepared at different conditions (spectra 2-4) and in comparison with the luminescence of perfect GaP bulk single crystals (1). Please see explanations in the text below.

Our unique collection of the long-term ordered perfect GaP single crystals gives opportunities to find deep fundamental analogies in properties of the perfect single crystals and nanoparticles [13, 14] as well as to predict and to realize in nanoparticles and perfect bulk crystals new interesting properties and applications. More detailed analyses and discussion of these results will be published.

## 3 CONCLUSIONS

Nanoparticles of GaP have been prepared using yellow P by mild aqueous low temperature synthesis. The spectra of PL, RLS, and XRD together with TEM images of the nanoparticles prepared under different conditions have been compared with each other as well as with those from bulk single crystals, that gives a good opportunity to find after the relevant investigation of different regimes and components for hydrothermal reactions the best performance in framework of this type of the nanoparticles synthesis. The uniform GaP nanoparticles having after

severe ultrasonic treatment and a number of other operations improving the quality of the nano-suspension a bright luminescence at room temperature in a broad band with maximum at 3 eV have been used in preparation of the nanocomposites described in [1].

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