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# Advanced Light Emissive Device Structures

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Additional information is available at the end of the chapter

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## 1. Introduction

This Chapter contains our latest achievements on organic and inorganic light emitters for display and waveguide applications. Two simultaneous efforts are described and analyzed. The first is the application of some transparent polymers to photoactive device structures. The second area focuses on the fabrication of optoelectronically-important structures based on GaP nanoparticles and their composites. The choice of materials are further complementary since they each are considered candidates for use in all optical circuits with commercial interest for light emitters, waveguides, converters, accumulators and other planar, fiber or discrete micro-optic elements.

Three objectives have been fulfilled and are reported here: 1) the development of new technologies for the preparation of nanocrystalline composite and GaP films; 2) the fabrication of novel optical planar light emissive structures for light emissive devices based on GaP/polymers nanocomposites; and 3) the generalization of experimental results from light emissive GaP bulk crystals, nanoparticles and nanocomposites.

Photoluminescence (PL), Raman light scattering (RLS), X-ray diffraction (XRD), atomic force and transmission electron microcopies (AFM and TEM) and other diagnostic methods have been used to characterize quality of GaP bulk and nanocrystals, GaP/polymers nanocomposites and to evaluate emissive efficiency of the obtained device structures. New solutions based on growth technique with use of modern analytical techniques were applied for growth and monitoring of semiconducting and composite films and fibers.

One of the main results described in the present Chapter is the creation and investigation of nanocomposite films based on GaP nanoparticles inserted into optically transparent polymers to prepare unique light emissive devices for optoelectronic applications. Different polymers were tested that combine the processability and durability of engineering

thermoplastics with suitable for GaP nanoparticles optical, electrical, thermal, and environment resistant properties.

Perfect single crystals from our unique collection of pure and doped GaP single crystals [1-25] compared with GaP nanoparticles prepared by us [26-31] serve as a standard yielding fundamental new knowledge and insights into semiconductor optical physics. Elaborating optimal methods of fabrication of GaP nanoparticles and their light emissive composites with compatible polymers [32-36] we use our own experience and literature data [37-39]. Due to considerable efforts in the past, including our contribution also, GaP has received significant attention as a material for use in a wide range of important modern optoelectronic devices including photodetectors, light emitters, electroluminescent displays and power diodes as well as being a model material with which to investigate the fundamental properties of semiconductors.

These two components of the composites, GaP and specially selected polymers, were unified based on their compatibility with the light emission spectral region as well as in their eventual integration into all optical circuits where bulk crystals or nanocrystals of GaP have been of commercial interest mainly for fiber and planar light emissive and micro-optic elements.

We hope our device structures obtained with application of accumulated for years results in their optics and technology [1-36, 41-43] will have significant commercial value because they present a new optical medium and product.

## **2. Development of technology for growth of GaP nanocrystals**

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

This activity is the important milestone in the creation of the nanocomposites for advanced light emissive device structures because GaP nanoparticles having the necessary luminescent and electroluminescent properties and compatible with a polymer matrix is a key element of these structures. We hope the described here some details and parameters of the technological processes used for fabrication of GaP nanocrystals with the improved and necessary for concrete application characteristics of luminescence will be useful in further elaboration of the relevant optoelectronic devices.

The quality of GaP nanoparticles was improved using mild aqueous synthesis and different colloidal reactions of Ga and P sources in toluene [26-38]. We used these methods taking into account that success of our activity depends on optimal choice of the types of chemical reactions, necessary chemicals and their purity, conditions of the synthesis (control accuracy, temperature, pressure, duration, etc.), methods and quality of purification of the nanocrystals, storage conditions for nanoparticles used in the further operations of fabrication of the GaP/nanocomposites.

Ultrasonication and ultracentrifugation have been applied during the synthesis and selection of nanoparticles to increase their quality and to select them on dimensions.

The relevant spectra of photoluminescence and Raman light scattering, X-ray diffraction and electron microscopy of the nanoparticles prepared under different conditions have been compared with each other as well as with those from bulk crystals. Thoroughly-prepared powders and suspensions of the nanoparticles have been used for preparation of GaP film nanocomposites on the base of different polymers compatible with the nanoparticles on optical and mechanical properties.

## 2.1. Equipment for fabrication of nanoparticles, fluoropolymers and nanocomposites

The equipment for fabrication of fluoropolymers and polymer nanocomposites has been elaborated by the author (JB) from Clemson University during our joint activity on light emissive structures. This equipment and approaches were applied to our specific needs without any serious modification.

### 2.1.1. Equipment for sublimation of phosphorus

It was found the synthesis on the base of white phosphorus gives the best quality of GaP nanoparticles. Due to the known prohibition for free sale of white phosphorus we have elaborated the facilities for its preparation using sublimation of its red modification (see Figure 1).

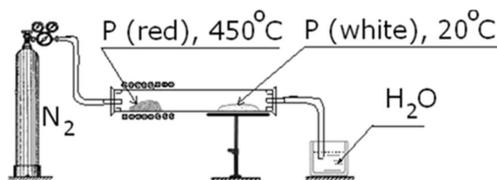


Figure 1. Preparation of white phosphorus.

The device is the silica tube, which is hermetic to the air, and is heated from one end while the P vapor is transferred by a neutral gas (nitrogen or argon) environment at the other cooled end of the tube where it is condensed there to form white phosphorus. After completion of the process the white phosphorus can be removed; the tube must be immersed into a water bath that to avoid inflammation of phosphorus in air.

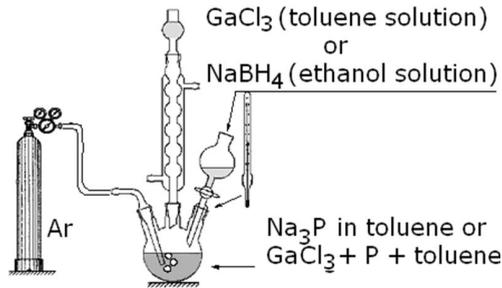
The obtained white phosphorus must be stored as a water suspension. Then this suspension by melting in boiled water is turned into the substance using in the synthesis of GaP nanoparticles.

### 2.1.2. Equipment for hydrothermal and colloidal synthesis

A new model of autoclave for the hydrothermal synthesis of GaP nanoparticles from the appropriate chemical solutions has been established given the requisite high temperatures (up

to 500°C) for the organic solvents using  $\text{GaCl}_3 \cdot 6\text{H}_2\text{O}$  and white phosphorus as precursors. Software for the process of synthesis at the temperature control and regulation with the accuracy of 0.1°C has been developed.

The key part of the method are the chemical reactions at high temperature and pressure. The reactor here is a hollow hermetic teflon cylinder. The necessary temperature (125°C, 200°C) inside the cylinder is obtained by its heating, while the pressure – by evaporation of water.



**Figure 2.** Equipment for preparation of GaP nanocrystals on the base of  $\text{NaBH}_4$  or  $\text{Na}_3\text{P}$ .

The equipment for colloidal synthesis of GaP nanocrystals using  $\text{NaBH}_4$  or  $\text{Na}_3\text{P}$  in toluene is shown in Figure 2.

## 2.2. Elaboration of technologies for fabrication of GaP nanoparticles

In 2005 the authors developed methods to fabricate GaP nanoparticles [26]. So, the technology and properties of the nanoparticles obtained in 2005-2006 and later [27, 28] are a good reference point for comparison to the new data provided herein.

More recently the authors [31] have concentrated on low temperature methods to synthesize GaP nanoparticles with improved luminescent characteristics. These methods are considerably different from those of other standard high temperature methods.

The first samples of GaP nanoparticles having a distinct luminescence at room temperature were obtained by hydrothermal method from aqueous solutions at relative low temperature (120-200°C). This method is discussed in Subsection 2.2.1. It was found that the composition of the nanoparticles corresponds to stoichiometric GaP.

The colloidal method provides a good opportunity to control the conditions of the synthesis, to decrease power inputs and to increase quality of nanoparticles concerning their purity and uniformity of their dimensions. In actuality, the single parameter, which may be controlled in the other methods, is the temperature, while using colloidal methods one can control nucleation of nanoparticles as well as velocity of their growth. The other important advantage of the colloidal method is the ability of so called “capping”; that is to isolate nanoparticles from each other, to prevent their agglomeration during storage, simultaneous-

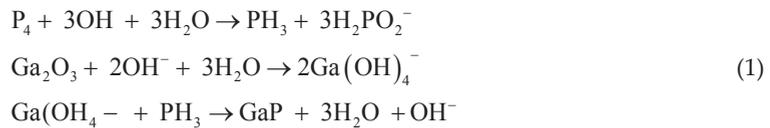
ly inhibiting their further growth. Therefore, we have elaborated the methods of GaP nanocrystals colloidal synthesis using  $\text{NaBH}_4$  and  $\text{Na}_3\text{P}$  compounds (Subsections 2.2.2 and 2.2.3).

### 2.2.1. Hydrothermal method of synthesis of GaP nanocrystals

Noted here are only essential details of the aqueous syntheses of GaP nanoparticles prepared at different temperatures and reaction conditions.

Using the literature data noted above the first nanocrystalline samples of GaP [26] have been prepared. The first aqueous prepared, relatively monodisperse, well crystallized GaP nanocrystallites, exhibiting pronounced quantum confinement effect have been presented in [27]. The relevant reactions were carried out in an aqueous solution at 120-160°C. A typical synthesis was as follows: 35,0 ml  $\text{H}_2\text{O}$ , 1,0 g  $\text{Ga}_2\text{O}_3$ , 1,0 g  $\text{NaOH}$ , 2,0 g white phosphorus were added to a 50 ml Teflon –lined autoclave, and 1,5 g  $\text{I}_2$  then was added. The autoclave was kept at 120-160°C for 8 hrs and then cooled to room temperature.

GaP nanoparticles were obtained in an alkali solution, taking advantage of the reaction of  $\text{Ga}(\text{OH})_4^-$  with  $\text{PH}_3$  which was produced from white phosphorus dispersed in alkali solution:



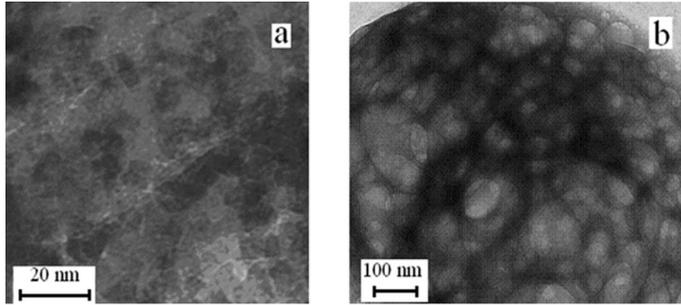
The yield of GaP in alkali solution is only about 12%. In order to improve the yield of GaP iodine was added to induce the reaction with white phosphorus, based on follow process:



The X-ray powder diffraction patterns of the as-prepared products indicated to the zinc blend structure of GaP with  $a = 5.43 \text{ \AA}$ . Average crystallite size estimated by the Scherrer equation are about 5 nm for GaP nanocrystals [27].

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

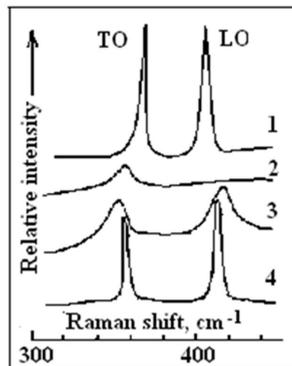
$\text{NaOH}$  pellets were dissolved in distilled water.  $\text{Ga}_2\text{O}_3$ , red or white phosphorus powder and  $\text{I}_2$  were mixed and added to the  $\text{NaOH}$  solution. The mixed solution was then placed into an autoclave and heated in an oven for 8 hours at 125 or 200°C. After the completion of heating the autoclave was taken out of the oven and cooled. The obtained powder was filtered, washed with ethanol,  $\text{HCl}$  and distilled water 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 industrial and specially grown and aged GaP single crystals also were used [1, 24].



**Figure 3.** 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.

The instruments employed for Raman light scattering and luminescence measurements included spectrographs interfaced to a liquid nitrogen-cooled detector and an argon ion laser or lamp excitation sources. Raman scattering spectra was obtained at room temperature by excitation with 514.5 nm radiation. Luminescence was excited by UV light of the lamps or the N<sub>2</sub> laser nanosecond pulses at wavelength 337 nm and measured at room temperature [25-28].

Figure 3 shows the TEM images of GaP nanoparticles obtained by the aqueous synthesis. The washed, thoroughly ultrasonicated and dried nanopowder contains mainly single 10nm nanoparticles (Figure 3a), obtained from the initial clusters with the dimensions of the order of 100 nm (Figure 3b).



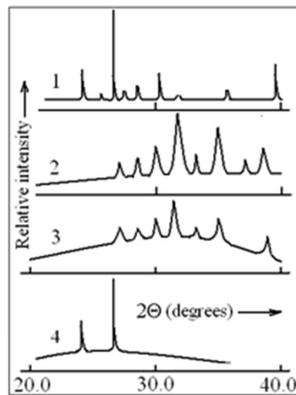
**Figure 4.** Raman light scattering from GaP nanoparticles of different treatment (spectra 2-4) in comparison with perfect GaP bulk crystals (spectrum 1).

Spectrum 2: Not thoroughly treated powder of nanoparticles prepared using red phosphorus at 200°C. Spectrum 3: Thoroughly treated GaP nanoparticles prepared using red phosphorus at 200°C. Spectrum 4: Nanoparticles prepared on the base of white P by low temperature syntheses.

Figure 4 shows the Raman light scattering spectra from GaP nanoparticles prepared using white or red P in mild aqueous synthesis at increased or low temperatures and ultrasonically treated.

In the colloidal method of the synthesis freshly prepared white phosphorus was used and ultrasonicated in toluene. Here the mixture for the reaction of the synthesis consists of  $\text{GaCl}_3 \cdot n\text{H}_2\text{O}$  diluted in toluene and dry  $\text{NaBH}_4$ . One of 2 fractions of different colors obtained in the synthesis was removed by rinsing in ethanol and water while the next one, containing the nanoparticles, was treated in a high-speed ultracentrifuge.

The characteristic GaP Raman lines from aged GaP single crystals (Figure 4, spectrum 1) and from the nanoparticles prepared using white P at low temperature (Figure 4, spectrum 4) were narrow and intense whereas, nanoparticles prepared from red P at higher temperatures (Figure 4, spectra 2 and 3) were weak and broad; the especially weak and broad spectrum exhibits not thoroughly washed powder (please see spectrum 2).

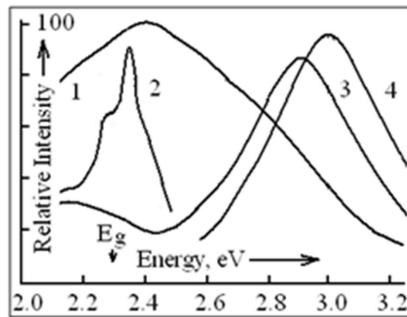


**Figure 5.** X-ray diffraction from GaP nanoparticles. 1. White phosphorus, using low temperature syntheses, well-treated powder. 2. White P, not the best performance and powder treatment. 3. Red phosphorus, the best result. 4. Perfect GaP bulk crystal.

In Figure 5 one can see x-ray diffraction from the GaP nanoparticles prepared at different conditions using red or white 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 white phosphorus exhibited clear and narrow characteristic lines like those obtained from perfect GaP bulk single crystals taken from our unique collection of long-term (app. 50 years) ordered GaP single crystals (Figure 5, spectra 1 and 4). Contrary to that, nanoparticles prepared using red phosphorus or less-than-optimum conditions showed broad and weak characteristic lines (Figure 5, spectra 2 and 3).

Any luminescence was absent in newly-made industrial and our freshly prepared crystals but it was bright in the same app. 50 years aged crystals (Figure 6, spectrum 1; the features of luminescence in the perfect aged crystals please see in [16-25]). Initial results on luminescent properties of GaP nanoparticles [26] confirmed the preparation of GaP nanoparticles

with dimensions of between 10-100 nm and 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 (Figure 6, spectrum 2). The nanoparticles obtained from the reaction with white P at low (125°C) temperature exhibit bright broad band spectra considerably shifted to UV side [27, 28, 36] (Figure 6, 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 (Figure 6, spectrum 3), but thorough ultrasonic treatment gives an opportunity to get the pure fraction of nanoparticles with the spectrum 4 having the maximum at 3 eV.



**Figure 6.** 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.

With these results, one can compare the properties of GaP nanoparticles with those of bulk single crystals grown in the 1960s or, approximately, 50 years ago [1-25]. The authors have investigated their optical and mechanical properties [16-25] in the 1960s, 1970s, 1980s and 1990s. Due to a significant number of defects and a highly intensive non-radiative recombination of non-equilibrium current carriers, initially luminescence from the freshly prepared undoped crystals could be observed only at the temperatures 80K and below. Today, luminescence is clearly detected in the region from 2.0 eV and until 3.0 eV at room temperature (see Figure 6, 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.

Our unique collection of long-term-ordered perfect GaP single crystals provides opportunities for deep fundamental analogies between perfect single crystals and nanoparticles [29-31] as well as to predict and to realize in nanoparticles and perfect bulk crystals new and interesting properties and applications as the advanced light emissive elements of relevant

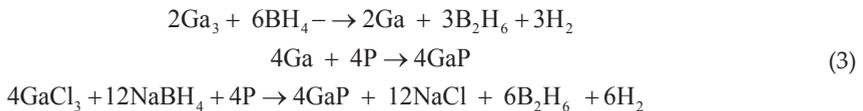
device structures. More detailed analyses and discussion of these results can be found in the references cited above and will be further published.

### 2.2.2. Synthesis of GaP nanocrystals on the base of NaBH<sub>4</sub> compound

In the method employed here, NaBH<sub>4</sub> was used as a deoxidizer during the synthesis in the solvent – toluene, where the sources of Ga and P (white phosphorus) have been dissolved (GaCl<sub>3</sub>) or suspended. NaBH<sub>4</sub> can be used also due to its high solubility in ethanol. The ethanol solution of NaBH<sub>4</sub> was introduced into the process of the synthesis during 5 hours, controlling the velocity of its introduction at the moderate heating up to 70°C.

White-yellow precipitates were the result of the synthesis. The precipitate was rinsed multiple times in toluene, removing the remaining P and GaCl<sub>3</sub>, and then in water, removing the water-soluble species such as NaCl. The centrifugal separation from the solvent has been used for extraction of the final precipitate having a lemon color.

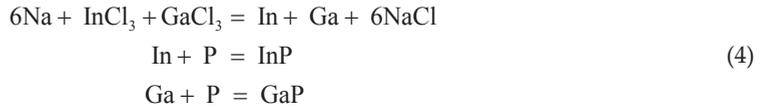
One can suppose the following scheme for the GaP synthesis:



The last reaction is the closing one, including creation of NaCl, which can be easily removed with deionized water. The main problem of the described synthesis is the exclusion Ga metal particles in the precipitate. The problem is controlled via the rate of Ga ion deoxidation, depending on temperature, the types of solvent and deoxidizer. Using low (~1 mL/min) rate of introduction of NaBH<sub>4</sub> ethanol solution into the process helps to avoid the metal Ga creation.

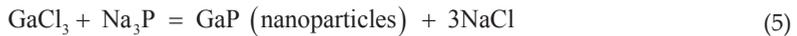
### 2.2.3. Synthesis of GaP nanocrystals on the base of Na<sub>3</sub>P

For the preparation of Na<sub>3</sub>P we used elementary Na, white P and the mixture of InCl<sub>3</sub>/GaCl<sub>3</sub> (4 wt% InCl<sub>3</sub> + 96 wt% GaCl<sub>3</sub>). The main experimental procedures can be described as follows: a 5.2 g mixture of GaCl<sub>3</sub> and InCl<sub>3</sub> was dissolved in 150 ml of xylene. Then, 2 g of sodium and 0.9 g of white phosphorus were added into the solution. The solution was stirred at 100°C for 10 hrs. After the reaction, the product was filtered for 3 times in xylene and 3 times in deionized water. The resultant powders were dried in vacuum at 60–80°C for 2 hrs. All the above mentioned manipulations were conducted in high purity nitrogen (99.999%) atmosphere in a glove box. Lastly, three equal parts of the product was heated respectively to 300°C, 480°C and 600°C for 1 hr in pure nitrogen (99.999%) flows. The reactions can be expressed as:

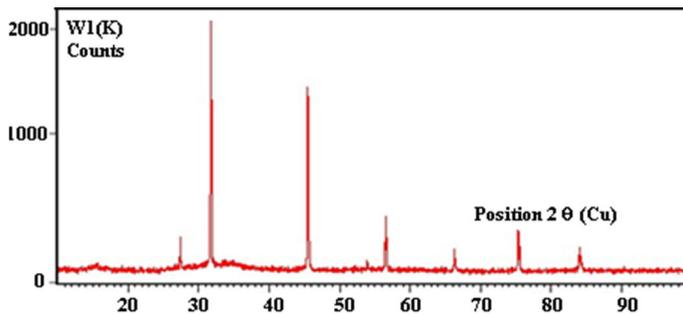


As the result the GaP nanoparticle aggregation was obtained. In a glove box, previously purged with dry nitrogen, 1.2 g of white phosphorus ( $\text{P}_4$ ) and 1.7 g of sodium (Na) were placed in 100 mL of distilled dimethylbenzene in an Erlenmeyer flask. The mixture was then stirred, heated to  $120^\circ\text{C}$  and maintained at that temperature for 10 hrs. A black fragmented product,  $\text{Na}_3\text{P}$ , was obtained. About 10 g of gallium (Ga) pellets were added to a quartz tube with one sealed end. The tube was purged with dry nitrogen and then heated gently. A chlorine gas flow through the melting metal was put in place at a rate until all the gallium reacted. The product - gallium chloride ( $\text{GaCl}_3$ ) was formed. In the glove box, 6.5 g of  $\text{GaCl}_3$  was dissolved in 100 mL of distilled dimethylbenzene in an Erlenmeyer flask. The solution was stirred and heated to  $100^\circ\text{C}$ . Then 2.5 g of  $\text{Na}_3\text{P}$  was added to the Erlenmeyer flask and the mixture was heated at  $100^\circ\text{C}$  with continuous stirring for 2.5 hr. After cooling, the mixture was filtered and washed with water.

The alternative method for preparation of GaP nanocrystals is interaction of  $\text{GaCl}_3$  and  $\text{Na}_3\text{P}$ :



In this method the stoichiometric ratio of Na (99,9%) and P (99,995%) is placed in the reactor with the Ar inert atmosphere. The reaction of preparation of  $\text{Na}_3\text{P}$  goes between melted Na and dispersed white P at  $110^\circ\text{C}$  in boiling toluene under intense stirring. This violent reaction must be supported at the necessary conditions ( $110^\circ\text{C}$  and intense stirring) for 5 hrs. As the result we have the black suspension of  $\text{Na}_3\text{P}$ :



**Figure 7.** XRD spectrum of GaP nanocrystals prepared on the base of  $\text{Na}_3\text{P}$  and  $\text{GaCl}_3$ .

According to elaborated by us technology [28, 31] the synthesis of GaP nanocrystals goes in the toluene solvent between dissolved ( $\text{GaCl}_3$ ) and dispersed ( $\text{Na}_3\text{P}$ ) initial chemicals at  $80^\circ\text{C}$  under ultrasonic machining for 5 hrs, creating a black-brown precipitate, which must be rinsed multiple times in toluene (removal of P and  $\text{GaCl}_3$ ) and water (removal of the soluble matter like NaCl). A high speed centrifuge must be used for separation of the precipitate. The resultant material must not be cleaned; its purity depends only on the purity of the initial components.

The XRD spectrum of GaP nanocrystals prepared using  $\text{Na}_3\text{P}$  and  $\text{GaCl}_3$  in toluene is presented in Figure 7. One can observe the characteristic (111), (220) and (311) reflections for GaP. However, there are some extraneous lines of the low intensity, probably, from NaCl,  $\text{NaPO}_3$  and showing that purification of GaP nanoparticles was not enough. The extraneous lines of the other than GaP components can be seen also in the spectra of GaP nanoparticles obtained by the method of Energy Dispersion X-ray Analysis (EDAX).

In conclusion we note that the growth of GaP nanocrystals is the key element in the creation of nanocomposite for advanced device structures because, in spite of the lack of the concrete parameters and conditions of synthesis in the relevant literature sources, all the necessary data for the preparation of GaP nanoparticles are provided herein.

Thus, nanoparticles of GaP have been prepared using white P by mild aqueous low temperature synthesis and 2 methods of colloidal chemistry. 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, from hydrothermal and colloidal reactions in toluene were presented. Uniform GaP nanoparticles, following ultrasonic treatment yielded a bright luminescence at room temperature with a broad band with maximum at 3 eV and have been used to prepare GaP/polymer nanocomposites.

### **3. Development of methods of incorporation of the GaP nanoparticles into polymers**

Polyglycidyl methacrylate (PGMA), polyglycidyl methacrylate-co-polyoligoethyleneglycol methacrylate (PGMA-co-POEGMA) and biphenyl vinyl ether (BPVE) polymers were used to synthesize GaP nanocomposites suitable for light emissive luminescent device structures. Some other polymers, dielectrics and with high electric conductivity, will be also investigated in the process of preparation of this Chapter and used for elaboration of light emissive device structures.

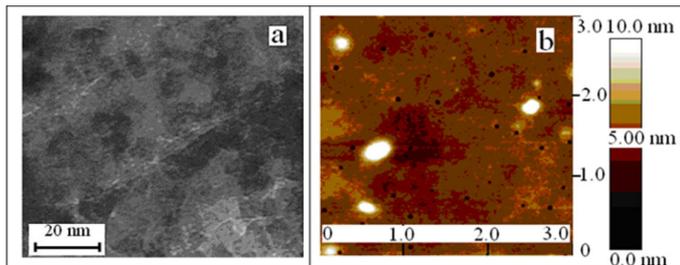
Film nanocomposites of good quality with very bright and broad-band luminescence have been prepared. Quality and surface morphology of the nanocomposite films was studied in ambient air using AFM in tapping mode on a Dimension 3100 (Digital Instruments, Inc.) microscope while luminescence of the nanocomposites films deposited by dip-coating from a suspension in water-ethanol mixture solution on the surface of a silica substrate was excited by the  $\text{N}_2$  laser nanosecond pulses at wavelength 337 nm and measured at room temperature.

The nanocomposites on the base of the noted above polymers were used for preparation and test of film light emissive device structures.

Thickness of the polymer composite film was within 250-300 nm defined from AFM scratch experiment. The following procedures have been used in the fabrication of the nanocomposites:

1. GaP powder was ultrasonicated in methylethylketone (MEK) using Branson 5210 ultrasonic bath. Then, PGMA was added to the MEK solution. GaP to polymer ratio was less than 1:10.
2. GaP powder was dispersed in water-ethanol mixture (1:1 volume ratio) and ultrasonicated using Branson 5210 bath for 120 min. Then, PGMA-co- POEGMA was added in the form of water-ethanol mixture (1:1 volume ratio) solution. GaP to polymer ratio was less than 1:3. Nanocomposite films were deposited on quartz slides via dip-coating;
3. GaP powder was dispersed in the biphenyl vinyl ether/dichloromethane (BPVE/DCM) solution; the solution was stirred and filtered from the excess of the powder. A few mL drops of the settled solution were casted onto silicon wafer.

More details on preparation and characterization of our GaP/polymers nanocomposites can be found in [31-36].



**Figure 8.** TEM image of GaP thoroughly ultrasonicated and dried nanoparticles obtained by mild aqueous synthesis (a) and AFM topography image of the GaP/PGMA nanocomposite (b).

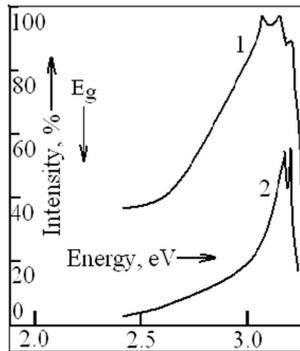
Figure 8a shows the TEM images of GaP nanoparticles obtained by the aqueous synthesis. One can see GaP nanoparticles, having characteristic dimensions less than 10 nm. The washed, thoroughly ultrasonicated and dried nanopowder contains mainly single nanoparticles, while the same powder obtained without ultrasonic treatment consists of the clusters with the dimensions of the order of 100 nm.

Figure 8b shows the AFM topography images of the GaP/PGMA film nanocomposite deposited by dip-coating from a suspension in water-ethanol mixture solution on the surface of a silica substrate. The AFM images demonstrated that no significant aggregation was caused by the polymerization. In general, individual particles were observed.

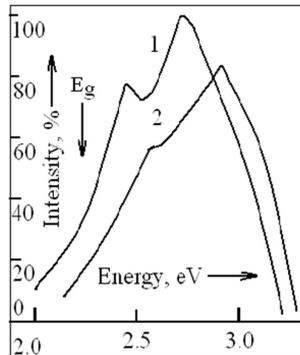
The thoroughly washed, ultrasonicated and dried nanopowders obtained by mild low temperature aqueous synthesis from white P as well as their specially prepared suspensions

have been used for fabrication of blue light emissive GaP nanocomposites on the base of some optically and mechanically compatible with GaP polymers. The relevant luminescence spectra are presented in Figures 9 and 10.

Figure 9 shows the spectra for GaP/PGMA-co-POEGMA nanocomposites. Comparing the results for the nanocomposites prepared from GaP powder or suspension (Figure 9, spectra 1 and 2 respectively), it was established that the best quality have the nanocomposites obtained from the nanoparticles stored as a suspension in a suitable liquid (see spectrum 2).



**Figure 9.** Spectra of luminescence from GaP/ PGMA-co-POEGMA nanocomposites. Nanoparticles have been prepared using white P by mild aqueous synthesis and stored as the dry powder (spectrum 1) or suspension in a liquid (spectrum 2).



**Figure 10.** Luminescence spectra of 2 GaP/BPVE nanocomposites produced on the base of 2 parties of GaP nanoparticles prepared using different conditions.

According to our measurements, the matrix polymers PGMA-co-POEGMA or BPVE used in this work provide no contribution to the spectra of luminescence of the based on these matrixes GaP nanocomposites presented in Figures 9 and 10, so, the nanocomposite spectra co-

incide with those obtained from the relevant GaP powders or suspensions. We note that in the GaP/BPVE nanocomposite the position of the luminescent maximum can be changed between 2.5 – 3.2 eV and the brightness is 20-30 more than in the PGMA and PGMA-co-POEG-MA matrixes. We explain the broadening of the luminescence band and the shift of its maximum to low photon energies in luminescence of the nanocomposite based on the GaP powder in Figure 9, spectrum 1, by the presence of the nanoparticles with the dimensions of 10-100 nm in the powder. Meanwhile, suspensions containing the 10 nm nanoparticles exhibit pronounced quantum confinement effects since this diameter equals the Bohr diameter of the bound exciton in GaP.

Figures 9 and 10 present a clear image of the quantum confinement effect in the GaP nanoparticles. In accord with our data [28-30] the shift is about a few tenths of eV and, obviously, it is impossible to explain only through this effect the dramatic 1 eV enhancement to the region of luminescence at 300 K on the high-energy side of the spectrum.

In order to explain this interesting phenomenon we postulate that the nanocrystals, much like the ideal long-term ordered bulk GaP single crystals, exhibit this huge increase in blue-shifted luminescence due to: (a) negligibly small influence of defects and non-radiative recombination of electron-hole pairs and very high efficiency of their radiative annihilation, (b) high perfection of nanocrystal lattice, and (c) high transparency of nanocrystals due to their small dimensions for the light emitted from high points of the GaP Brillouin zones, for instance, in the direct transitions  $\Gamma_c^1 - \Gamma_v^{15}$  between the conductive and valence bands with the photon energy at 300°K equal to 2.8 eV [40] and (d) high efficiency of this so called “hot” luminescence.

Our first attempts to prepare GaP nanoparticles [26] yielded room temperature luminescence with maximum shifted only to 2.4 eV in comparison with the new maximum at 3.2 eV. It confirms significant achievements in technology of GaP nanoparticles and GaP/polymers nanocomposites. On the base of these improved technologies for preparation of GaP nanoparticles and GaP/polymer nanocomposites we can change within the broad limits the main parameters of luminescence and expect to create a framework for novel light emissive device structures using dramatic 1 eV expansion of GaP luminescence to UV region.

The film device structures demonstrate broadband luminescence in the region from UV until yellow-red with controlled width and position of maximum with the luminous intensity up to 1 cd compared with industrial light emitting diodes.

#### **4. Comparison of properties of the GaP nanocrystals and perfect bulk single crystals**

Jointly with Refs. [1-31] this section is a generalization of the results on long-term observation of luminescence, absorption, Raman light scattering, and microhardness in bulk semiconductors in comparison with some properties of the best to the moment GaP nanocrystals. We show that the combination of these characterization techniques elucidates the evolution of these crystals over the course of many years, the ordered state brought about by pro-

longed room-temperature thermal annealing, and the interesting optical properties that accompany such ordering. We demonstrate that long-term natural stimuli improve the perfection of our crystals, which can lead to novel heterogeneous systems and new semiconductor devices with high temporal stability.

Our unique collection of long-term ordered perfect GaP single crystals gives opportunities to find deep fundamental analogies in properties of the perfect single crystals and nanoparticles as well as to predict and to realize in nanoparticles and perfect bulk crystals new interesting properties and applications.

The long-term ordering of doped GaP and other semiconductors has been observed as an interesting accompanying process, which can only be studied in the situation when one has a unique set of samples and the persistence to observe them over decade time scales.

Any attempt to accelerate the above noted processes, for instance, through annealing of GaP at increased temperatures cannot be successful because high-temperature processing results in thermal decomposition (due to P desorption) instead of improved crystal quality. Therefore successful thermal processing of GaP can only take place at temperatures below its sublimation temperature, requiring a longer annealing time. Evaluated within the framework of the Ising model the characteristic time of the substitution reaction during N diffusion along P sites in GaP:N crystals at room temperature constitutes 10 -15 years [5]. Hence, the observations of luminescence of the crystals made in the sixties and the nineties were then compared with the results obtained in 2009-2012 in closed experimental conditions.

The pure and doped GaP crystals discussed herein were prepared nearly 50 years ago. Throughout the decades they have been used to investigate electro- and photoluminescence (PL), photoconductivity, bound excitons, nonlinear optics, and other phenomena. Accordingly, it is of interest also to monitor the change in crystal quality over the course of several decades while the crystal is held under ambient conditions.

More specifically, since 2005, we have analyzed the optical and mechanical properties of single crystalline Si, some III-V semiconductors, and their ternary analog  $\text{CdIn}_2\text{S}_4$ , all of which were grown in the 1960s. Comparison of the properties of the same crystals has been performed in the 1960s, 1970s, 1980s, 1990s [1-12], and during 2000s [13-25] along with those of newly made GaP nanocrystals [26-28] and freshly prepared bulk single crystals [19-23]. We improved in the preparation of GaP nanocrystals the known methods of hydrothermal and colloidal synthesis taking into account that success of our activity depends on optimal choice of the types of chemical reactions, necessary chemicals and their purity, conditions of the synthesis (control accuracy, temperature, pressure, duration, etc.), methods and quality of purification of the nanocrystals, storage conditions for nanoparticles used in the further operations of fabrication of the GaP/nanocomposites.

Single crystals of semiconductors grown under laboratory conditions naturally contain a varied assortment of defects such as displaced host and impurity atoms, vacancies, dislocations, and impurity clusters. These defects result from the relatively rapid growth conditions and inevitably lead to the deterioration of the mechanical, electric, and optical properties of the material, and therefore to rapid degradation of the associated devices.

Different defects of high concentration in freshly prepared GaP single crystals completely suppress any luminescence at room temperature due to negligible quantity of free path for non-equilibrium electron-hole pairs between the defects and their non-radiative recombination, while the quantum theory predicts their free movement in the field of an ideal crystal lattice. The long-term ordered and therefore close-to-ideal crystals demonstrate bright luminescence and stimulated emission repeating behavior of the best nanoparticles with pronounced quantum confinement effects. These perfect crystals due to their unique mechanical and optical properties are useful for application in top-quality optoelectronic devices as well as they are a new object for development of fundamentals of solid state physics, nanotechnology and crystal growth.

Continuing generalization of data on improvement of properties from semiconductor GaP:N crystals prepared nearly 50 years ago and their convergence to the behavior of GaP nanoparticles, here we discuss only the most interesting for fundamentals of solid state physics and application in optoelectronics and photonics data.

1. Over time, driving forces such as diffusion along concentration gradients, strain relaxation associated with clustering, and minimization of the free energy associated with properly directed chemical bonds between host atoms result in ordered redistribution of impurities and host atoms in a crystal.
2. We observe in the long-term ordered GaP:N single crystals a new type of the crystal lattice, where host atoms occupy their equilibrium positions, while impurities divide the lattice in the short chains of equal length in which the host atoms develop harmonic vibrations.
3. The nearly half-centennial evolution of the GaP:N luminescence and its other optical and mechanical properties are interpreted as the result of both volumetrically ordered N impurities and the formation of an ordered crystal-like bound exciton system. The highly ordered nature of this new host and excitonic lattices increases the radiative recombination efficiency and makes possible the creation of advanced non-linear optical media for optoelectronic applications.

Taking into account the above-mentioned results, a model for the crystal lattice and its behavior at a high level of optical excitation for 40-year-old ordered N-doped GaP have been suggested [3]. At relevant concentrations of N, the anion sub-lattice can be represented as a row of anions where N substitutes for P atoms with the period equal to the Bohr diameter of the bound exciton in GaP (approximately 10 nm). At some level of excitation, all the N sites will be filled by excitons, thereby creating an excitonic crystal which is a new phenomenon in solid-state physics and a very interesting object for application in optoelectronics and nonlinear optics [3, 30].

The perfect ordered GaP:N crystals demonstrate uniform luminescence from a broad excitonic band instead of the narrow zero-phonon line and its phonon replica in disordered and partly ordered (25-year-old) crystals due to the ordered crystals having no discrete impurity level in the forbidden gap. To the best of our knowledge, the transformation of a discrete level within the forbidden gap into an excitonic band is observed for the first time. In this

case, the impurity atoms regularly occupy the host lattice sites and affect the band structure of the crystals, which is now a dilute solid solution of GaP-GaN rather than GaP doped by occasionally located N atoms.

As noted previously, the luminescence of fresh doped and undoped crystals could be observed only at temperatures below about 80 K. The luminescence band and lines were always seen at photon energies less than the value of the forbidden gap (2.3 eV). Now, after 50 years, luminescence of the long-term-ordered bulk crystals similar to the GaP nanocrystals [27-31] is clearly detected in the region from 2.0 eV to 3.0 eV at room temperature [13-25]. We believe, in the long-term-ordered bulk crystals this considerable extension of the region of luminescence at 300°K to the high-energy side of the spectrum is due to: (a) a very small concentration of defects, (b) low contribution of nonradiative electron-hole recombination, (c) considerable improvement of crystal lattice, (d) high transparency of perfect crystals, and (e) low probability of phonon emission at indirect transition.

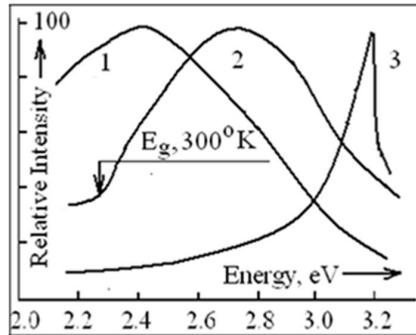
Earlier, in freshly prepared crystals we observed a clear stimulated emission from a GaP:N resonator at 80 K [4] as well as so called superluminescence from the GaP single crystals. Presently, our ordered crystals have a bright luminescence at room temperature that implies their perfection and very lower light losses. Currently we demonstrate [19, 20, 24, 29, 30] that the stimulated emission is developed even at room temperature by direct electron-hole recombination of an electron at the bottom of the conduction band with a hole at the top of the valence band and the LO phonon absorption.

We also have demonstrated the considerable improvement of quality of GaP nanocrystals as the result of elaboration of an optimal for them nanotechnology. Figure 11 compares the luminescence spectra of our long-term (up to 50 years) ordered GaP single crystals (spectrum 1) to that from high quality GaP nanoparticles [27-31] and their GaP nanoparticles/polymers nanocomposites [34-36].

The best quality GaP nanoparticles have been prepared by hydrothermal or colloidal synthesis from white phosphorus at decreased temperature (125°C) and intense ultrasonication.

Comparing the results for the nanocomposites prepared from GaP powder or suspension (Figure 11, spectra 2 and 3 respectively), it was established that the maximum shift to ultraviolet and the best quality in general have the nanocomposites obtained from the nanoparticles stored as a suspension in a suitable liquid.

Nanocrystals stored as dry powder demonstrate rather broad luminescent band with maximum at 2.8 eV (Figure 11, spectrum 2), while the nanocrystals of about 10 nm sizes, thoroughly separated and distributed in a suspension, that prevent their coagulation, mechanical and optical interaction, exhibit bright narrow-band luminescence with maximum at 3.2 eV, approximately 1 eV above the position of the absorption edge in GaP at 300°K (Figure 11, spectrum 3). The thoroughly washed, ultrasonicated and dried nanopowders as well as their specially prepared suspensions have been used for fabrication of blue light emissive GaP nanocomposites on the base of some optically and mechanically compatible with GaP polymers.



**Figure 11.** Luminescence of perfect bulk GaP single crystals (1) in comparison with the luminescence of GaP nanoparticles and GaP/polymers nanocomposites (2-3). Nanoparticles prepared from white P by mild aqueous or colloidal synthesis at decreased temperature, stored as the dry powder (spectrum 2) or suspension in a liquid (spectrum 3).

According to our measurements, the matrix polymers PGMA-co-POEGMA or BPVE used in this work provide no contribution to the spectra of luminescence of the based on these matrixes, so, the nanocomposite spectra coincide with those obtained from the relevant GaP powders or suspensions.

We note that in the GaP/BPVE nanocomposite the position of the luminescent maximum can be changed between 2.5 – 3.2 eV and the brightness is 20-30 more than in the PGMA and PGMA-co-POEGMA matrixes. We explain the broadening of the luminescence band and the shift of its maximum to low photon energies in luminescence of the nanocomposite based on the GaP powder by presence in the powder of the nanoparticles with the different dimensions between 10-100 nm. Meanwhile, the nanocomposites on the base of the suspensions containing only approximately 10 nm nanoparticles, exhibit bright luminescence with maximum at 3.2 eV due to high transparency of 10 nm nanoparticles for these high energy emitted photons and pronounced quantum confinement effects since this diameter equals the Bohr diameter of the bound exciton in GaP.

In accordance with previous data [27-31, 34-36] the shift due to the quantum confinement effects is about a few tenths of eV and, obviously, it is impossible to explain only through this effect the dramatic 1 eV expansion of the region of luminescence at 300 K to the high-energy side of the spectrum.

In order to explain this interesting phenomenon we postulate that the nanocrystals, much like the ideal long-term ordered bulk GaP single crystals, exhibit this huge increase in blue-shifted luminescence due to: (a) negligibly small influence of defects and non-radiative recombination of electron-hole pairs and very high efficiency of their radiative annihilation, (b) high perfection of nanocrystal lattice, and (d) high transparency of nanocrystals due to their small dimensions for the light emitted from high points of the GaP Brillouin zones, for instance, in the direct transitions  $\Gamma_1^c - \Gamma_{15}^v$  between the conductive and valence bands with the photon energy at 300°K equal to 2.8 eV [40] and (e) high efficiency of this so called "hot" luminescence.

Our first attempts to prepare GaP nanoparticles [26] yielded room temperature luminescence with maximum shifted only to 2.4 eV in comparison with the new maximum at 3.2 eV. It confirms significant achievements in technology of GaP nanoparticles and GaP/polymers nanocomposites. On the base of these improved technologies for preparation of GaP nanoparticles and GaP/polymer nanocomposites we can change within the broad limits the main parameters of luminescence and expect to create a framework for novel light emissive device structures using dramatic 1 eV expansion of GaP luminescence to UV region.

Semiconductor nanoparticles were introduced into materials science and engineering mainly that to avoid limitations inherent to freshly grown semiconductors with a lot of different defects. The long-term ordered and therefore close to ideal crystals repeat behavior of the best nanoparticles with pronounced quantum confinement effect. These perfect crystals are useful for application in top-quality optoelectronic devices as well as they are a new object for development of fundamentals of solid state physics.

#### 4.1. Conclusions

This study of long-term convergence of bulk- and nanocrystal properties brings a novel perspective to improving the quality of semiconductor crystals. The unique collection of pure and doped crystals of semiconductors grown in the 1960s provides an opportunity to observe the long term evolution of properties of these key electronic materials. During this almost half-centennial systematic investigation we have established the main trends of the evolution of their optoelectronic and mechanical properties. It was shown that these stimuli to improve quality of the crystal lattice are the consequence of thermodynamic driving forces and prevail over tendencies that would favor disorder. For the first time, to the best of our knowledge, we have observed a new type of the crystal lattice where the host atoms occupy their proper (equilibrium) positions in the crystal field, while the impurities, once periodically inserted into the lattice, divide it in the short chains of equal length, where the host atoms develop harmonic vibrations. This periodic substitution of a host atom by an impurity allows the impurity to participate in the formation of the crystal's energy bands. It leads to the change in the value of the forbidden energy gap, to the appearance of a crystalline excitonic phase, and to the broad energy bands instead of the energy levels of bound excitons. The high perfection of this new lattice leads to the abrupt decrease of non-radiative mechanisms of electron-hole recombination, to both the relevant increase of efficiency and spectral range of luminescence and to the stimulated emission of light due to its amplification inside the well arranged, defect-free medium of the crystal. The further development of techniques for the growth of thin films and bulk crystals with ordered distribution of impurities and the proper localization of host atoms inside the lattice should be a high priority.

This long-term evolution of the important properties of our unique collection of semiconductor single crystals promises a novel approach to the development of a new generation of optoelectronic devices. The combined methods of laser assisted and molecular beam epitaxies [41-43] will be applied to fabrication of device structures with artificial periodicity;

together with classic methods of crystal growth, can be employed to realize impurity ordering that would yield new types of nanostructures and enhanced optoelectronic device performance.

Our long-term ordered and therefore close to ideal crystals repeat behavior of the best nanoparticles with pronounced quantum confinement effect. These perfect crystals are useful for application in top-quality optoelectronic devices as well as they are a new object for development of fundamentals of solid state physics.

For the first time we also show that well-aged GaP bulk crystals as well as high quality GaP nanoparticles have no essential difference in their luminescence behavior, brightness or spectral position of the emitted light. The long-term ordered and therefore close to ideal crystals repeat behavior of the best nanoparticles with pronounced quantum confinement effect. These perfect crystals are useful for application in top-quality optoelectronic devices as well as they are a new object for development of fundamentals of solid state physics.

Especially important for application in new generation of light emissive devices is the discovered in framework of the Project [31] dramatic expansion of luminescence region in GaP perfect bulk single crystals as well as in the best prepared GaP nanocrystals and based on them composites with transparent polymers. The broad discussion and dissemination of our results will stimulate development of our further collaboration with reliable partners from the USA, Italy, Romania, France and other countries.

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