# We are IntechOpen, the world's leading publisher of Open Access books
# Built by scientists, for scientists

4,800
Open access books available

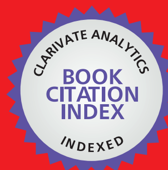
122,000
International authors and editors

135M
Downloads

154
Countries delivered to

Our authors are among the
TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities




WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Chapter 1

# Properties of GaP Studied over 50 Years

Sergei L. Pyshkin and John Ballato

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/67852

**Abstract**

A unique set of GaP semiconductor samples studied for over 50 years has exhibited significant improvement in their properties through the formation of the perfect host crystal lattice and the N-impurity crystal superlattice. This chapter reviews this evolution of properties and discusses their novel utility in advanced optoelectronic devices. More specifically, nitrogen-doped gallium phosphide (GaP:N) crystals that were originally prepared in the 1960s were theorized to form an excitonic crystal (1970s), and the best methods of their bulk, film, and nanoparticle crystal growth have subsequently been developed. The excitonic crystals yield novel and useful properties including enhanced stimulated emission and very bright and broadband luminescence at room temperature, which have been observed. These results provide a new approach to the selection and preparation of "perfect" materials for optoelectronics and offer a unique opportunity to realize a new form of solid-state host—the excitonic crystal—as a high-intensity light source with low thresholds for nonlinear optical effects.

**Keywords:** long-term evolution of crystal properties, excitonic crystal, close to ideal crystals

## 1. Introduction

Described herein are studies initiated by one of the authors (SLP) in 1961. Further studies on the same samples were conducted in the later 1960s through 1970s, then again in the 1980s, 1990s, and 2000s making these a very unique set of semi-centennial observations [1–34, 40–42].

One of the most important findings of this study was the observation, first recognized in the 1980s, of a significant improvement over time in the properties of GaP crystals under ambient temperature and pressure. In particular, it was found that ordering of host and impurity

INTECH
open science | open minds

© 2017 The Author(s). Licensee InTech. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. (cc) BY

atoms improved over time as did the GaP mechanical properties, luminescence with tunable spectral characteristics, and nonlinear optical effects, not observable in the freshly prepared (imperfect) crystals.

Over time, as confirmed by 50 years of experiments on the same samples, 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, results in an ordered redistribution of impurities and host atoms in the crystal. In the particular case of GaP, as well as other compounds possessing highly volatile components, attempt to accelerate these processes through annealing at increased temperatures cannot be successful due to the potential for thermal decomposition (in GaP—due to P desorption). Accordingly, successful thermal processing of these compounds can only take place at temperatures below the sublimation temperatures of their volatile constituents, requiring a longer annealing time. For instance, as evaluated in 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 15–20 years [2]. Hence, the observations of highly excited luminescence and some other phenomena in the crystals made in the 1960–1970s and in the 1980–1990s were then compared with the results obtained in 2005–2014 under similar experimental conditions.

The long-term ordering of doped GaP and other semiconductors has been observed as an important accompanying process, which only can be studied using the same unique set of samples and decade time scales. More specifically, the optical and mechanical properties of single crystalline GaP and some other semiconductors, also grown in the 1960s, have been analyzed. Comparison of the properties of the same crystals was performed in the 1960s, 1970s, 1980s, and 1990s [1, 3–17] along with those of newly made GaP nanocrystals [18–20] and freshly prepared bulk single crystals [21–24]. Jointly with Refs. [25, 26, 31–34], this review provides a generalization of the results on these long-term observations of luminescence, absorption, Raman light scattering, and microhardness of the bulk single crystals in comparison with the same properties of the high-quality GaP nanocrystals. It is shown that the combination of these characterization techniques elucidates the evolution of these crystals over the course of many decades. It also clarifies the ordered state brought about by prolonged room-temperature thermal annealing, and the useful optical properties that accompany such ordering. It is demonstrated that long-term natural stimuli that improve the perfection of crystals prevail over other processes and can lead to novel heterogeneous device systems and new semiconductor devices with high temporal stability.

In this chapter, we summarize more than 50 years of results of the study of evolution of the properties of the GaP crystals stored under normal conditions and, on this basis, we propose a new approach to resource-saving production of optoelectronic materials and unique devices based on them.

## 2. Bulk perfect crystals

The method to grow gallium phosphide crystals from GaP solution melt was chosen due to the significant temperature reduction of the process and the presence of large amounts of

solvent which dramatically reduce impurities from the container. Note that lamellar crystals grown from this solution melt are the most convenient and economical material in the manufacture of many semiconductor devices.

The influence of the following factors on the quality of the grown single crystals has been investigated: (1) quantity and chemical nature of impurities; (2) geometric shape of the container and conditions of heat rejection; (3) accuracy of the temperature control; and (4) cooling rate and the law of heat-sink cooling.

The solution-melt method of GaP growth is described in detail in Refs. [1, 3, 7]. The focus here is only on the most essential details of the crystal growth.

Synthesis, alloying, and crystallization of Ga-P mixture were combined in a single cycle. Influence of impurities on the growth of GaP crystals was investigated using the highest-purity industrially produced materials at that time (1960) in the former USSR. The growth of the crystals was conducted in a sealed quartz container that was introduced into the programmable furnace with a vibrating mount to agitate the mixture of Ga, P, and any chosen dopant. This agitation was performed to facilitate chemical reaction between components and to avoid a possible explosion of the container in dangerous temperature points of the process of mass crystallization.

In order to study the form and quality of growing crystals, the crystallization process could be interrupted at any temperature below the point of liquidus. This interruption was achieved with the help of a specially designed growth container and its programmable heating furnace, which allow to stop the change of temperature of the solution melt, to identify and examine grown to this time crystals (see details in Refs. [1, 3]).

The solution, carefully heated to slightly over 400°C, was held at this temperature for about 2 h to transform the red phosphorus precursor into its white form. Then, the heating process may be smoothly prolonged until a temperature of about 1200°C is reached, which exceeds the liquidus point for 5% P solution in Ga (1123°C) and creates appropriate conditions for Ga-P reactions. After about 1–3 h, the samples are gradually cooled at a rate of 30°C/h to 600–700°C and then the furnace is turned off and naturally cooled to room temperature.

The following impurities were doped into the GaP individually: Cu, Zn, Cd, In, Si, Ge, Sn, S, Se, Te, Ni, Cr, Fe, Co, Sm, La, Gd, and $Sm_2O_3$. Typical features of the doped GaP crystals (size, color, polarity, lamellar structure, twinning, the dislocation structure, and others) were compared with similarly grown but undoped crystals.

It was found [1, 3] that the properties of the crystals depend on the chemical nature as well as on the quantity of the selected impurities. Their small admixtures did not significantly change the form of the crystals, while significant change of the crystallization environment composition created changes in forms of growth. It was also found that the following factors most significantly influenced the morphology of GaP crystals grown from the Ga-P solution: (a) the degree of supersaturation, which depends on the temperature of the solution and (b) its first derivative with time; the conditions of the heat crystallization removal and the accuracy of the temperature control in the solution.

Changing crystallization conditions, mainly the rate of cooling of the melt, significantly affects the morphology of crystals. Accordingly, the increase of the cooling rate thus reduced the size of the crystals, but the dislocation density was not changed and was primarily determined by the concentration and chemical nature of the impurities. The number of crystals having isometric forms increased with decreasing of cooling rate resulting in the simultaneous improvement of the quality of the crystal surface. Uneven removal of heat from the walls of the container led to the formation of up to 30-mm crystal needles elongated in the direction of the heat removal.

Significant impact on the crystal quality provides more accurate temperature control. The crystals obtained with the accuracy of temperature control ±0.5°C had the perfect planes (111), low dislocation density, and dimensions that were two to three times larger than the crystals obtained at the same conditions, but with the accuracy of ±5°C. Crystals reached 25 mm in length and had the dislocation density of $\sim 10^3$ $cm^{-2}$, which is significantly less than that of the crystals obtained with low accuracy of the temperature control [1, 3].

Based on the findings of this investigation, let us now present an overview of the growth of lamellar GaP crystals. The first crystals, having the form of dendritic needles with the length of the order of 5 mm and thickness of 0.15 mm, were grown at the temperature of 1107°C, which is approximately 16°C of undercooling. The crystals represent thin plates in the form of rhombs, triangles, or hexagons. The twinning on the transverse cross sections was observed at the study of microsections and cleaved facets. It turned out that the lamellar GaP crystals contain the plane of twinning, parallel to the planes (111) [1, 22].

The growth process of lamellar crystals can be formally divided into two components: the tangential growth in the plane (111) and layer-by-layer growth in the direction normal to the plane (111). Because the ratio of Ga and P atoms differed significantly from the stoichiometry, it is assumed that diffusion is the process that determines the rate of growth. Accepting the two-stage model of lamellar crystal growth, let us consider the ratio of the contributions of the tangential growth in the plane (111) and layer-by-layer growth in the direction normal to the plane (111). The growth in the tangential direction is limited by diffusion and by the size of the previous layer, that is, is determined by the initial conditions and the shape and size of the plates, formed during the cooling of the solution melt 10–20° below the point of liquidus. Since the formation of the initial crystals occurs in a very short time, the growth in the tangential direction is difficult to control, as it is in the case of the dendritic crystal growth. The growth in the direction normal to the plane (111) is sensitive to the fluctuations of the degree of supersaturation, resulting from the thermal motion of atoms and temperature fluctuations. In general, the better the homogeneity and perfection of the surface of the lamellar GaP crystals, the lesser the ratio of the time necessary for the formation of flat embryos on it, to the time for which the embryo is created on the next plane. The latter, obviously, in an extreme extent depends on fluctuations of the degree of supersaturation in different points of the growing plane and at different points in time. With the deterioration of precision temperature control, the number of fluctuations increases and low-quality crystals grow in the conditions of "entanglement" of the above-noted characteristic times. Small fluctuations of supersaturation also are probably the cause of twinning planes. Increase of the accuracy of temperature

regulation promotes some reduction in the number of twins, and this fact also confirms the notable influence of fluctuations on the twinning [1, 3, 34].

Thus, deteriorations of quality or shape of defects of GaP plates during their growth from Ga-P melt solution were observed in the following cases: (1) at a considerable increase of concentration of impurities in the GaP solution and dependently on the chemical nature of the chosen impurity and (2) at the change of the crystallization conditions, namely, at the sufficient deterioration of the cooling velocity control or in the case of nonuniform heat removal from the container for the crystal growth.

Processes for the formation of dendritic needles and their transformation to platelet crystals take place over a small temperature and time interval. As a result, they are hard to control, while crystal growth is easily controlled in the direction normal to the plate (111), due to the sensitive nature of velocity of the solution cooling and accuracy of the temperature control [1, 3].

The above-stated results imply that only high-quality and carefully controlled growth equipment will yield the highest-quality GaP crystals. However, despite these precautions, the subsequent text shows how to considerably increase the quality and utility of freshly prepared GaP crystals.

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

GaP nanoparticles have been prepared using white P under mild aqueous low-temperature synthesis conditions using two colloidal methods from mixtures of $GaCl_3$•$nH_2O$ and dry $NaBH_4$ or $Na_3P$ and $GaCl_3$ diluted in toluene. Details are provided in Refs. [17–20].

Uniform GaP nanoparticles formed following ultrasonic and other treatments were found to exhibit improved quality in their colloidal stability and brightness of luminescence at room temperature, which is found to be broadband with a maximum at 3 eV. Also discussed is their use in GaP/polymers nanocomposites for light-emissive device structures [28, 30, 31].

Photoluminescence, spontaneous Raman scattering, and X-ray diffraction, together with high-resolution electron microscopy of the nanoparticles prepared under different conditions, were compared with those from bulk single crystals.

For the first time to the best of our knowledge, it is shown 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 emitted light.

While bulk and thin-film GaP has been successfully commercialized for many years, their application in nanocomposites as a new optical medium has only recently received attention. This section reviews 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 exhibit important luminescent and electroluminescent properties and are compatible with selected polymer matrices.

The quality of GaP nanoparticles was improved using mild aqueous synthesis and different colloidal reactions of Ga and P sources in toluene [26–37]. Ultrasonication and ultracentrifugation were applied during the synthesis and selection of nanoparticles to increase their quality and to control the size of the nanoparticles.

In 2005, the authors developed methods to fabricate GaP nanoparticles [18]. So, the technology and properties of the nanoparticles obtained in 2005–2006 and later [27–30] are a good reference point for comparison of the new data provided herein [31].

The first samples of GaP nanoparticles having a distinct luminescence at room temperature were obtained by hydrothermal method from aqueous solutions at a relatively low temperature (120–200°C). 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 the 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 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 the so-called "capping," that is, to isolate nanoparticles from each other, to prevent their agglomeration during storage, simultaneously inhibiting their further growth. Therefore, we have elaborated the methods of GaP nanocrystals colloidal synthesis using $NaBH_4$ and $Na_3P$ compounds.

## 4. 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. Film nanocomposites of good quality with high brightness and broadband luminescence were realized. The thickness of the polymer composite film was within 250–300 nm defined from atomic force microscope (AFM) 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 milliliter drops of the settled solution were casted onto silicon wafer.

More details on the preparation and characterization of our GaP/polymers nanocomposites can be found in Refs. [31, 33–36].

**Figure 1a** shows transmission electron microscope (TEM) images of GaP nanoparticles obtained from 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 1b** shows atomic force microscope (AFM) topographic 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 relevant luminescence spectra are presented in **Figures 2** and **3**.

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

According to our measurements, the matrix polymers PGMA-co-POEGMA or BPVE used in this work provide no contribution to the luminescence spectra of luminescence based on these matrixes GaP nanocomposites presented in **Figures 2** and **3**, so, the nanocomposite spectra coincide with those obtained from the relevant GaP powders or suspensions. It is noted that in the GaP/BPVE nanocomposite, the position of the luminescent maximum can be changed between 2.5 and 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 in **Figure 2**, spectrum 1, by the presence of the nanoparticles with the dimensions of 10–100 nm in the powder.

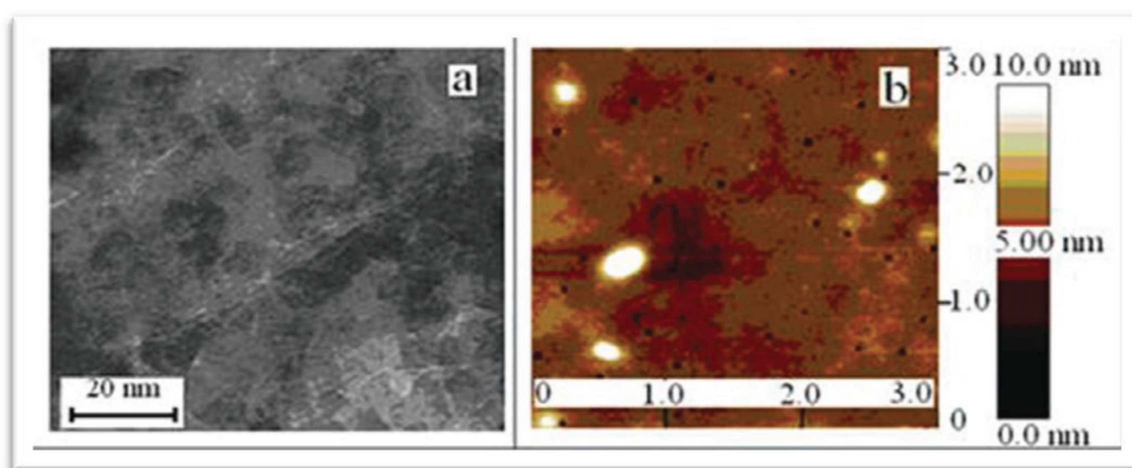



**Figure 1.** TEM image of GaP thoroughly ultrasonicated and dried nanoparticles obtained by mild aqueous synthesis (a) and AFM topography image of the GaP/PGMA nanocomposite (b) [17].

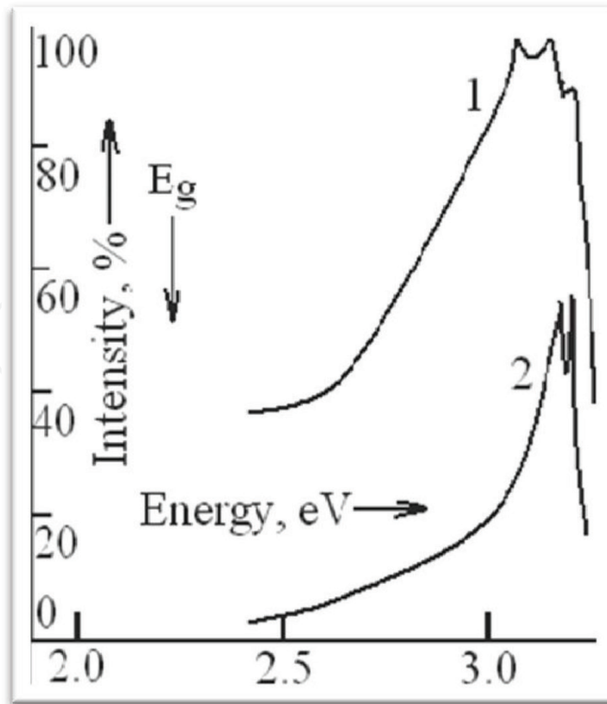



**Figure 2.** Spectra of luminescence from GaP/PGMA-co-POEGMA nanocomposites. Nanoparticles have been prepared using white P by mild aqueous synthesis and stored as the dry powder (spectrum 1) or suspension in a liquid (spectrum 2) [17].

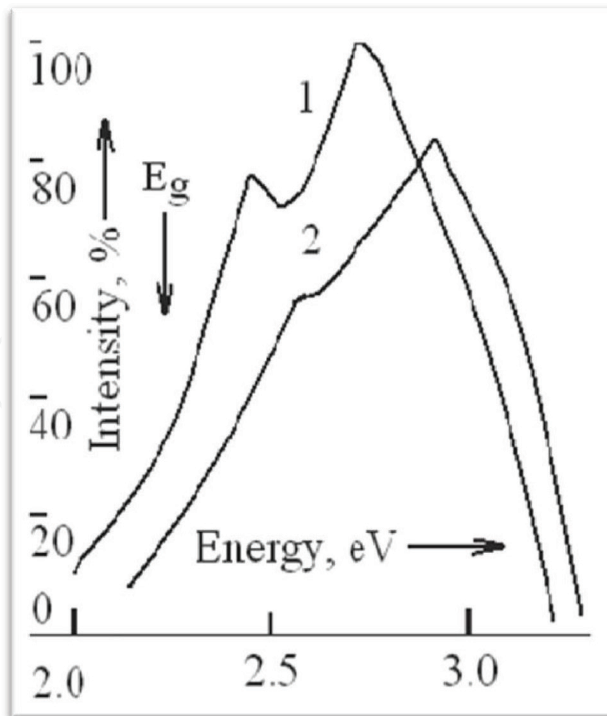



**Figure 3.** Luminescence spectra of 2 GaP/BPVE nanocomposites produced on the base of two parties of GaP nanoparticles prepared using different conditions [17].

http://dx.doi.org/10.5772/67852

**Figures 2** and **3** present a clear image of the quantum confinement effect in the GaP nanoparticles. In accord with our data, 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 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 $\Gamma^1{}_c$–$\Gamma^{15}{}_v$ between the conductive and valence bands with the photon energy at 300°K equal to 2.8 eV [39] and (d) high efficiency of this so-called "hot" luminescence. On the basis of these improved technologies for the preparation of GaP nanoparticles and GaP/polymer nanocomposites, we can control within broad limits the main parameters of luminescence and expect therefrom to create a framework for novel light-emissive device structures using this dramatic 1-eV expansion of GaP luminescence to the UV region.

Thus, the film device structures, elaborated by us, 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.

## 5. Optical properties of perfect, long-term-ordered GaP:N in comparison with freshly prepared crystals

Investigating gallium phosphide (GaP) crystals grown by the author in the 1960s, clear improvement of their optical and mechanical properties was noted for the first time only after 10–12 years. It was unusual and interesting in the situation when all inorganic nature around us usually deteriorates in time. Therefore, the decision was taken to investigate, to understand, and to use this phenomenon in the future. In short, the investigation process can be described as follows.

**Figure 4** provides a comparison of the evolution in luminescence spectra at low temperatures (80 K and below) from GaP:N over a period of 25 years. It is seen over this period zero-phonon line A of single N-impurity-bound excitons and their phonon replica are narrower in their line widths when compared to the freshly prepared single crystals. Further, as expected, zero-phonon line and replica in samples aged at room temperature for 25 years shift spectral position depending upon the concentration of N impurities (**Figure 4b**, spectra 1–3) according to Refs. [38, 39], while the same freshly prepared crystals exhibited broader luminescence line widths with increasing nitrogen content (**Figure 4b**, spectrum 4). These, along with other half-centennial findings, including modifications in luminescence kinetics, spontaneous Raman scattering, X-ray diffraction, absorption spectra, micro-hardness, and density of dislocations, that are reported elsewhere [1, 3–24], strongly suggest that close-to-ideal GaP:N crystals form over time due to the equally spaced disposition of N impurities instead of their chaotic distribution in the same freshly prepared crystals.

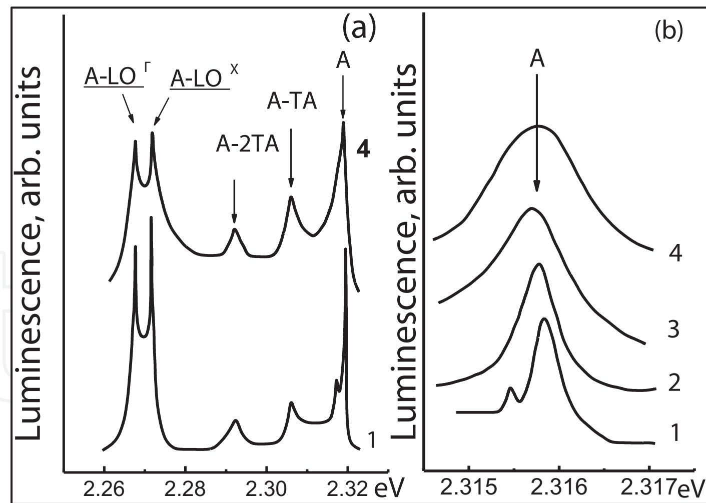



**Figure 4.** Evolution of the GaP:N luminescence with time and nitrogen concentration at the temperature of 15 K. (a) Zero-phonon line of the bound exciton A and its transversal acoustic (TA) and longitudinal optic (LO) phonon replica in as-prepared (4) and 25-year long-term-ordered (1) crystals. (b) Zero-phonon line A as a function of nitrogen (N) concentration. 1–3: 25-year-old crystals. 4: as-prepared. Curves 1 through 4 represent samples with nitrogen concentrations of $10^{17}$, $10^{18}$, $10^{19}$, and $10^{18}$ $cm^{-3}$, respectively [34].

As first noted in Ref. [23], these results suggest a new type of crystal lattice in which the host atoms occupy their proper (equilibrium) positions in the crystal, while the N impurities are periodically substituted into the lattice portion into short chains of equal length. According to the data obtained from Raman light scattering [10, 14], host atoms of this new lattice develop harmonic vibrations, and high degree of lattice perfection leads to an abrupt decrease in the non-radiative recombination and an increase of efficiency and spectral range of luminescence.

Stimulated emission of light in these temporally ordered crystals (**Figure 5b**) also is observed. As was shown in Ref. [23], the GaP:N crystals aged for at least 40 years possess no discrete

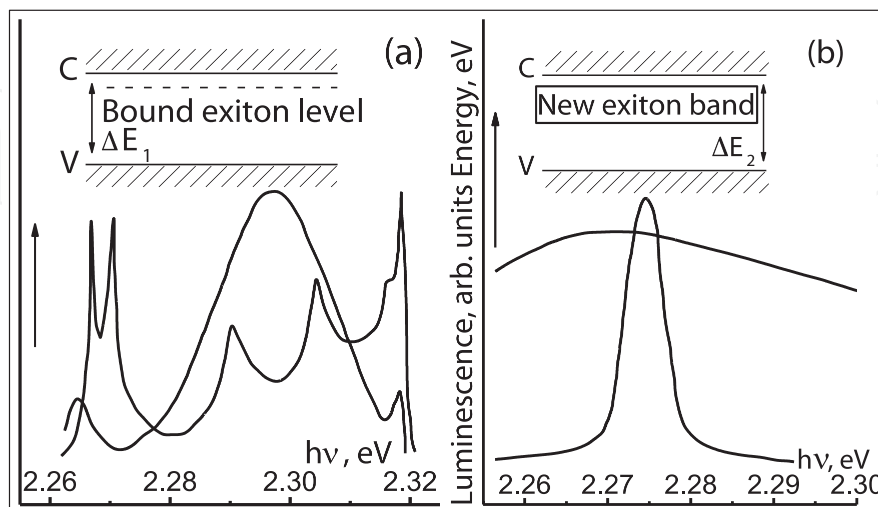



**Figure 5.** Luminescent spectra and schematic representation of the forbidden gaps ($\Delta E_1$, $\Delta E_2$) in the nitrogen-doped GaP aged for (a) 25 years and (b) 40 years [34].

impurity level for N-bound excitons in the forbidden gap. They also demonstrated a uniform luminescence from a broad excitonic band instead of the narrow zero-phonon line and its phonon replica as observed from the less-aged, 25-year-old crystals.

Thus, long-term-ordered GaP:N crystals demonstrate uniform bright 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. This is due to the fact that ordered crystals have no discrete impurity level in the forbidden gap. To the best of our knowledge, such transformation of a discrete level within the forbidden gap into an excitonic band (**Figure 5a, b**) 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 are now a dilute solid solution of GaP-GaN with regular disposition of N atoms instead of freshly prepared GaP doped by occasionally located N atoms. Note that the increase of luminescence excitation in case of partly ordered GaP:N (**Figure 5a**, dotted line) leads to a broad luminescence band as a result of bound exciton interaction [9], while in the case of perfectly ordered crystals (**Figure 5b**), one can see an abrupt narrowing of the luminescence band due to stimulated emission in defect-free crystals. Earlier, in freshly prepared crystals, we observed a clear stimulated emission from a GaP:N resonator at 80 K [5], as well as the so-called superluminescence from GaP single crystals having natural faceting. Presently, our ordered crystals have a bright luminescence at room temperature that implies their perfection and very low light losses. In our studies [14, 23], we demonstrate that the stimulated emission in long-term-ordered GaP is also developed even at room temperature by 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.

## 6. Comparison of optical properties of GaP:N nanocrystals and GaP perfect bulk single crystals

It is necessary to note that the very important for optoelectronics long-term ordering and considerable improvement of the semiconductor crystal lattice and accompanying phenomena have been discovered and observed over decade time scales only due to grown in 1960th [1, 3, 7] unique collection of samples and control of evolution of their properties for 50years. And up to now, this 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. Jointly with Refs. [3, 7, 9–17, 21–27, 31–34], this section is a generalization of the results on long-term observation of luminescence, absorption, and Raman light scattering in bulk semiconductors in comparison with some properties of the best to the moment GaP nanocrystals. Combination of these characterization techniques elucidates the evolution of these crystals over the course of many years, as well as the ordered state brought about by prolonged room-temperature thermal annealing, and the interesting optical properties that accompany such ordering. We demonstrate that long-term natural stimuli result in perfection of our crystals, which can lead to novel heterogeneous systems and new semiconductor devices with high temporal stability.

We further improved upon the preparation of GaP nanocrystals using the known methods of hydrothermal and colloidal synthesis [29–31].

The highest-quality GaP nanoparticles have been prepared using hydrothermal or colloidal synthesis from white phosphorus at a decreased temperature (125°C) and intense ultrasonication. It has been established that the maximum shift to ultraviolet and the best quality, in general, are from nanocomposites obtained from the nanoparticles stored as a suspension in a suitable liquid.

As noted earlier, different defects of high concentration in freshly prepared GaP single crystals completely suppress any luminescence at room temperature due to the 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. It was also shown 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.

**Figure 6** 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 and their GaP nanoparticles/polymers nanocomposites [15, 17]. Nanocrystals stored as dry powder demonstrate rather broad luminescent band with maximum at 2.8 eV (**Figure 6**, spectrum 2), while the nanocrystals of about 10-nm sizes, thoroughly separated and distributed in a suspension, which prevents their coagulation, mechanical, and optical interaction, exhibit bright narrow-band

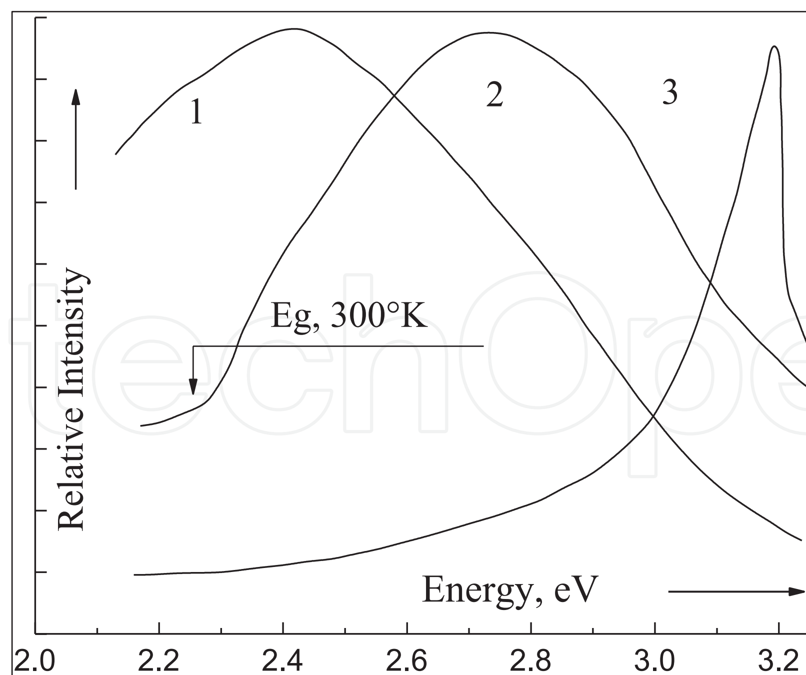



**Figure 6.** Luminescence of perfect bulk GaP single crystals (1) in comparison with the luminescence of GaP nanoparticles and GaP/polymers nano-composites (2, 3). Nanoparticles were prepared from white P by mild aqueous or colloidal synthesis at decreased temperature, stored as dry powder (spectrum 2) or suspension in a liquid (spectrum 3). Details can be found in Refs. [15, 17].

luminescence with maximum at 3.2 eV, approximately 1 eV above the position of the absorption edge in GaP at 300°K (**Figure 6**, spectrum 3).

The broadening of the luminescence band and the shift of its maximum to low-photon energies in the nanocomposite is explained based on the different dimensions (between 10 and 100 nm) of the GaP powder. Meanwhile, the nanocomposites on the basis 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 effect.

Our first attempts to prepare GaP nanoparticles [18, 27] yielded room-temperature luminescence with maximum shifted only to 2.4 eV in comparison with the achieved now new maximum at 3.2 eV achieved today. It confirms significant progress in the technology of GaP nanoparticles and GaP/polymers nanocomposites. On the basis of these improved approaches to prepare GaP nanoparticles and GaP/polymer nanocomposites, we can change the main parameters of luminescence within the broad limits, and to create a framework for novel light-emissive device structures using dramatic 1-eV expansion of GaP luminescence to UV region.

## 7. Excitonic crystal and its importance in optoelectronics

The role and application of bound excitons in nanoscience and technology are discussed in this section. Bound excitons are well studied in semiconductors, especially in gallium phosphide doped by nitrogen (GaP:N). Doping of GaP with N leads to isoelectronic substitution of the host P atoms by N in its crystal lattice and to the creation of the electron trap with a large capture cross section. Therefore, any non-equilibrium electron in the vicinity of the trap will be captured by N atom, attracting a non-equilibrium hole by Coulomb interaction and creating the bound exciton—short-lived nanoparticle with the dimension of the order of 10 nm (it is the Bohr diameter of bound exciton in GaP:N). Note that none of the nanotechnology methods are used in the creation or selection of dimensions of these nanoparticles—only natural forces of electron-hole interaction and electron capture by the traps are necessary for the creation of these nanoparticles. As a result, we get something like neutral short-lived atom analog—a particle consisting of heavy negatively charged nucleus (N atom with captured electron) and a hole. The so-called "zero vibrations" do not destroy possible solid phase of bound excitons having these heavy nuclei that give an opportunity to reach their crystal state—short-lived excitonic crystal.

Taking into account the abovementioned results, a model for the crystal lattice and its behavior at a high level of optical excitation for well-ordered N-doped GaP (**Figure 7**) can be suggested. At the relevant concentrations of N, the anion sublattice can be represented as a row of anions where N substitutes P atoms with the period equal to the Bohr diameter of the bound exciton in GaP (approximately 10 nm) (**Figure 7a**). At some level of excitation, all the N sites will be filled by excitons, thereby creating an excitonic crystal (**Figure 7b**), which is a new phenomenon in solid-state physics and a very interesting medium for application in optoelectronics and nonlinear optics [4, 15, 17, 25, 26, 32–34].

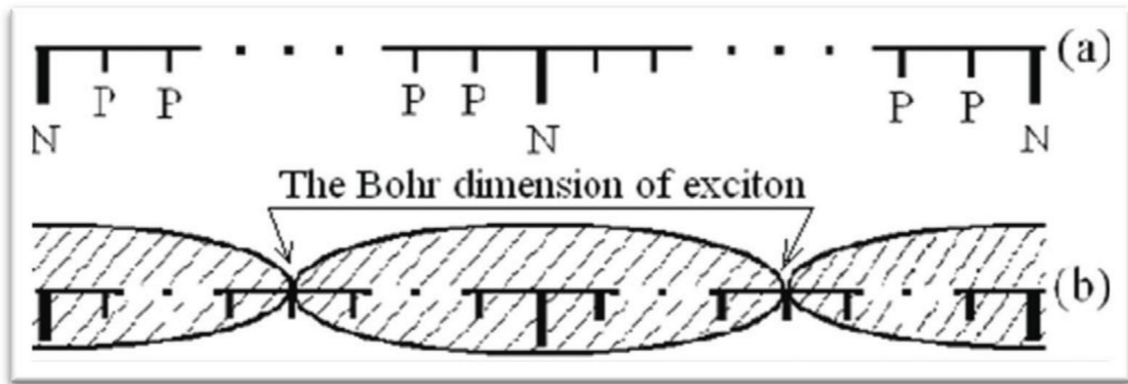



**Figure 7.** The models of the well-ordered GaP:N [34]. (a) The new type of crystal lattice with periodic substitution of N atoms for the host P atoms. (b) The excitonic crystal on the basis of this lattice. The substitution period is equal to the Bohr diameter of exciton (~100 Å), and optical excitation is enough for complete saturation of the N sublattice with non-equilibrium electron-hole pairs (please see details in Refs. [15, 17]).

Thus, using bound excitons as short-lived analogs of atoms and sticking to some specific rules, including the necessity to build the excitonic superlattice with the identity period equal to the bound exciton Bohr dimension in the GaP:N single crystal, we get a unique opportunity to create a new solid-state media—consisting of short-lived nanoparticles excitonic crystal, obviously, with very useful and interesting properties for application in optoelectronics, nanoscience, and technology.

## 8. Current approach to selection of materials for electronics and new prospects

The ability of matter to emit light of definite wavelengths and intensity depends on many factors; among them are the details of its band structure and crystal quality. Applied to light-emissive materials and device structures, the quality is characterized by the concentration of the defects damaging light emission due to non-radiative electron-hole recombination on these defects. The ways for minimization of expected losses of the light in non-radiative electron-hole recombination are (1) decrease of concentration of the defects in the material grown by an improved method; (2) considerable quality improvement of GaP crystal structure discovered by us during long-term (tens of years) ordering of the host and impurity atoms, and (3) application of nanocrystals with the dimensions less than the free paths of electrons and holes in the chosen light-emissive material.

Properties that can be used to achieve light emission at a definite spectral region include (1) selection of the material on the basis of its band structure peculiarities and the value of the forbidden gap, which as a rule sizes up the maximum value of the emitting photons; (2) doping of the selected material by impurities or, on the contrary, precise purification of the chosen material for the creation of new channels of light emission; and (3) selection of the temperature and/or excitation level that to change contribution of different channels into light emission due to their disappearance or saturation.

It is impossible or, at least, very difficult to realize all the above-noted possibilities in a single material. Therefore, the present technologies of light-emissive optoelectronics employ diverse range materials using very complicated and expensive technologies for their fabrication with the necessary application parameters. Down-selecting a set of various materials applied currently in optoelectronics at the maintenance or even improvement of their high parameters and quality is one of the most important goals for reduction in price and wide application in the practice of electronic devices. The most impressive demonstration of this approach would be the selection of a suitable material, the development of a peculiar technology of its preparation, its interesting properties and prospects for application in optoelectronics instead of a huge number of various materials and their technologies.

Sophisticated growth technique, knowledge of crystal growth mechanisms, of different processes, improving or deteriorating in time the prepared crystals, and the relevant comprehensive experience are necessary for the preparation of the perfect, free or almost free of contamination and doped GaP single crystals.

However, in the manufacture of artificial crystals, we are faced with the need to fabricate them for a very short time compared with the times for which naturally perfect crystals are grown. For example, a hundred years passes before the growing in the nature crystal acquires the dimensions necessary for its use as feedstock in jewelry making, while the commercial growth of moderately perfect semiconductors takes only a few hours. In such a short time, its own atom or dopant diffusing through the crystal usually cannot absolutely exactly occupy the places intended for them in ideal crystal lattice. This gives rise to lattice defects, which, in turn, hinder the achievement of perfect devices. Manufactured on the basis of such materials, greatly reduce their lifetime, as well as make it impossible manifestation of some very interesting and useful for the application of the effects observed in advanced materials. Significant levels of funds are spent on searching and implementing methods for creating materials, not existing in the nature, that can, even if in a narrow field of application and at short time service, replace the material with a perfect crystal lattice and the necessary concentration and location of dopants. Hence, there is an urgent need to develop methods for the creation of an ideal semiconductor material the required parameters for use in electronics. In this case, it will disappear or substantially decrease the need to develop a plurality of individual costly technology to produce a plurality of different materials with a limited resource and service applications, and as a very important result for any country involved in the production and use of electronic materials—a giant savings and the possibility of redeployment to other needs of funds spent on the production of low-quality materials and products.

Using the long-term-ordered perfect GaP or similar on behavior and properties material in electronic industry instead of current elaboration of very expensive and labor-consuming technologies for diverse materials with their limited application spectral region and other parameters, we get a big commercial, scientific, and technology advantage from their fabrication and application.

We hope that the methods based on the application of this long-term evolution of the important properties of our unique collection of semiconductor single crystals [31–34] as well as the combined methods of laser-assisted and molecular beam epitaxies [40–42] elaborated by us promise a novel approach to the development of a new generation of optoelectronic devices.

The epitaxial methods, elaborated by us [40–42], will be applied to the fabrication of device structures with artificial periodicity; together with classic methods of crystal growth, they can be employed to realize impurity ordering that would yield new types of nanostructures and enhanced optoelectronic device performance.

The long-term, tens of years ordered GaP, its artificial analogs, and nanoparticles have very interesting and properties for different application, which give an opportunity to apply them in optoelectronics with high economic effect instead of a lot of different compounds currently used in optoelectronics.

## 9. Conclusions

Thus, our half-of-a-century collection of results provides a new approach to the selection and preparation of perfect optoelectronics materials (please see references to this chapter) and a unique opportunity to realize a new form of solid-state host—the excitonic crystal [32–34]. These results confirm expedience of the efforts directed to the formation in GaP of the N-impurity superlattice having a lattice period equal to the bound exciton dimension. As noted in this chapter and the relevant references, high-quality material for industrial electronics can be prepared by storing freshly grown crystals for years in a special storage. Only old crystals with the attained necessary properties will then be annually retrieved for device fabrication, while new portions of fresh crystals will be placed for long-term ordering at room temperature, as is done with wines and fine liquors.

All of the results presented here and included in summary reviews [25, 26, 32–34] may sufficiently change the approach to the selection of materials necessary for electronics, and to make cheaper and simpler technology for the preparation of the selected materials and device structures on which they are based. This study of long-term convergence of bulk- and nanocrystal properties [15, 17] brings a novel perspective to improving the quality of semiconductor crystals. The author's unique collection of pure and doped crystals of semiconductors grown in the 1960s provides an opportunity to observe and understand the physics behind the long-term evolution of properties in these key electronic materials.

## Acknowledgements

The authors are glad to note that the broad discussion and dissemination of their joint results stimulate further collaboration with reliable partners from the USA, Russia, Italy, Romania, France, and other countries.

Prof. Sergei L. Pyshkin expresses his cordial gratitude to his teachers, world-known scientists late Profs Nina A. Goryunova, Nobel Prize Laureate Alexander M. Prokhorov, and academicians Rem V. Khokhlov and Sergei I. Radautsan. He is also very grateful to the US Department of State, Institute of International Exchange, Washington, DC, the US Air Force Office for Scientific

Research, the US Office of Naval Research Global, Civilian R&D Foundation, Arlington, VA, the US Science & Technology Center in Ukraine, to his colleagues and coauthors from Clemson University, SC, University of Central Florida, FL, Istituto di elettronica dello stato solido, CNR, Rome, Italy, Universita degli studi, Cagliari, Italy, Lomonosov Moscow State University, Joffe Physico-Technical Institute and State Polytechnical University, St. Petersburg, Ac. Scie. Institute of General Physics, Moscow, Russia, Institute of Applied Physics and Academy of Sciences of Moldova for support and attention to this protracted (1961 to present time) research.

## Author details

Sergei L. Pyshkin[1,2]* and John Ballato[2]

*Address all correspondence to: spyshkin@yahoo.com

1 Institute of Applied Physics, Academy of Sciences of Moldova, Kishinev, Moldova, Republic of Moldova

2 Clemson University, South Carolina, USA

## References

[1] Goryunova NA, Pyshkin SL, Borshchevskii AS, et al. Influence of impurities and crystallization conditions on growth of platelet GaP crystals. In: Symposium on Crystal Growth at the 7th International Crystallography Congress (Moscow, July 1966). N.N. Sheftal, editor, Journal of Growth of Crystals 1969; 8: 68-72, New York.

[2] Pyshkin SL, Radautsan SI, Zenchenko VP. Processes of long-lasting ordering in crystals with a partly inverse spinel structure. Journal of Soviet Physics – Doklady 1990; 35(4): 301-4.

[3] Pyshkin SL. Preparation and Properties of Gallium Phosphide. Ph.D. thesis 1967, State University of Moldova, Kishinev.

[4] Pyshkin SL, Zifudin L. Excitons in highly optically excited gallium phosphide. Journal of Luminescence 1974; 9: 302-8.

[5] Pyshkin SL (presented by Nobel Prize Laureate A.M. Prokhorov). Stimulated emission in gallium phosphide. Journal of Soviet Physics – Doklady 1975; 19: 845-6.

[6] Pyshkin S. Luminescence of GaP:N:Sm crystals. Journal of Soviet Physics of Semiconductors 1975; 8: 912-3.

[7] Pyshkin SL. Photoconductivity and luminescence of highly optically excited semiconductors. Dr.Sc. thesis 1978, Lomonosov Moscow State University.

[8] Pyshkin S, Anedda A, Congiu F, Mura A. Luminescence of the GaP:N Ordered System. Journal of Pure and Applied Optics 1993; 2: 499-502.

[9] Pyshkin S., Alberto Anedda. Time-Dependent Behaviour of Antistructural Defects and Impurities in Cd-In-S and GaP. Institute of Physics Conference Series 1998, Ternary and Multinary Compounds; 152, Section E: 785-789

[10] Pyshkin S, Ballato J, Chumanov G. Raman light scattering from long-term ordered GaP single crystals. Journal of Optics A: Pure and Applied Optics 2007; 9: 33-6.

[11] Pyshkin SL, Ballato J, Bass M, Turri G. Luminescence of long-term ordered pure and doped gallium phosphide. TMS Annual Meeting, Invited Talk at the Symposium: Advances in Semiconductor, Electro Optic and Radio Frequency Materials, March 9-13, New Orleans, LA. J. Electronic Materials 2008; 37(4): 388-95.

[12] Pyshkin SL, Ballato J, Bass M, Chumanov G. Time-dependent evolution of crystal lattice, defects and impurities in $CdIn_2S_4$ and GaP. Journal of Physica Status Solidi 2009; C(6): 1112-5.

[13] Pyshkin SL, Ballato J, Bass M, Turri G. Evolution of luminescence from doped gallium phosphide over 40 Years. Journal of Electronic Materials 2009; 38(5): 640-6.

[14] Pyshkin S, Ballato J. Evolution of optical and mechanical properties of semiconductors over 40 Years. Journal of Electronic Materials 2010; 39(6): 635-41.

[15] Pyshkin S, Ballato J. Long-term convergence of bulk- and nano-crystal properties. In:Optoelectronics – Materials and Technics, InTech – Open Access Publisher, ISBN 978-953-307-276-0; Chapter 19: 2011; 459-476.

[16] Pyshkin S. Ballato J. Dramatic expansion of luminescence region in GaP/polymer nano-composites. Supplemental Proceedings of the 2012 TMS Annual Meetings (Orlando, FL, USA, March 11-15); vol. 1: "Materials Processing and Interfaces": 2012; 353-359.

[17] Pyshkin S, John Ballato. Advanced light emissive device structures. In: Optoelectronics – Advanced Materials and Devices, S.L. Pyshkin and J. Ballato, editors, ISBN 978-953-51-0922-8, InTech – Open Access Publisher; Chapter 1: 2013; 1-24.

[18] Pyshkin S, Ballato J, Chumanov G, DiMaio J, Saha AK. Preparation and Characterization of Nanocrystalline GaP. Technical Proceedings of the 2006 NSTI Nanotech Conference; 3: 194-197.

[19] Pyshkin S, Ballato J, Chumanov G, Tsyntsaru N, Rusu E. Preparation and characterization of nanocrystalline GaP for advanced light emissive device structures. In: The 2010 NSTI-Nanotech Conference (Anaheim, CA) Proceedings: www.nsti.org, ISBN 978-1-4398-3401-5; vol. 1: 522-5.

[20] Pyshkin SL, Ballato J, Belevschii S, Rusu E, Racu A, Van DerVeer D. Synthesis and characterization of GaP nanoparticles for light emissive devices. In: The 2011 NSTI-Nanotech Conference, Boston, MA, June 13-16. Proceedings: www.nsti.org, ISBN 978-1 4398-7142-3; vol. 1, 327-30.

[21] Pyshkin SL, Ballato J, Bass M, Chumanov G, Turri G. Time-dependent evolution of crystal lattice, defects and impurities in $CdIn_2S_4$ and GaP. Physica Status Solidi 2009; C(6): 1112-5.

[22] Pyshkin S, Zhitaru R, Ballato J, Chumanov G, Bass M. Structural characterization of long-term ordered semiconductors. Proceedings of the 2009 MS&T Conference, International Symposium "Fundamentals & Characterization": 698-709.

[23] Pyshkin S, Ballato J, Bass M, Chumanov G, Turri G. Properties of the long-term ordered semiconductors. Suppl. Proceedings of the 2009 TMS Annual Meeting and Exhibition; 3: 477-84 (San Francisco, February 15-19, 2009).

[24] Pyshkin S, Ballato J, Chumanov G, Bass M, Turri G, Zhitaru R, et al. Optical and mechanical properties of long-term ordered semiconductors. Moldavian Journal of the Physical Sciences 2009; 8(3-4): 287-95. The 4th Int. Conference on Materials Science and Condensed Matter Physics, Kishinev, Sept 23-26, 2008.

[25] Pyshkin SL. Gallium Phosphide - New Prospect for Optoelectronics. J. Advances in Optoelectronic Materials (AOM), ISSN Online: 2327-7661, ISSN Print: 2327-767X); 2013; 1(4): 59-66.

[26] Pyshkin SL. Excitonic crystal and nanotechnology. Symbiosis Journal of Nanoscience & Technology: Open Access 2014; 1(2), 1-5. Available from http://symbiosisonlinepublishing. com/nanoscience-technology08.pdf

[27] Pyshkin S, John B. Advanced light emissive composite materials for integrated optics. Symposium: The Physics and Materials Challenges for Integrated Optics – A Step in the Future for Photonic Devices, Proc. of the 2005 MS&T Conference, Pittsburgh: 3-13.

[28] Pyshkin S, Ballato J, Luzinov I, Zdyrko B. Fabrication and characterization of the GaP/polymer nanocomposites for advanced light emissive device structures. The 2010 NSTI-Nanotech Conference; 1: 772-5. www.nsti.org, ISBN 978-1-4398-3401-5. Anaheim, CA, June 21-24, 2010.

[29] Pyshkin S, Ballato J, Chumanov G, Tsyntsaru N, Rusu E. Preparation and characterization of nanocrystalline GaP for advanced light emissive device structures. The 2010 NSTI-Nanotech Conference; 1: 522-5. www.nsti.org, ISBN 978-1-4398-3401-5.

[30] Pyshkin SL, Ballato J, Luzinov I, Zdyrko B. Fabrication and characterization of GaP/polymer nanocomposites for advanced light emissive device structures. Journal of Nanoparticle Research 2011; 13: 5565-70.

[31] Pyshkin SL. (Project Manager). Advanced Light Emissive Device Structures. STCU (www.stcu.int) Project 4610, 2009-2012.

[32] Sergei LP. Excitonic crystal, nanotechnology and new prospect for optoelectronics. The Open Optics Journal 2015; 9: 26-37.

[33] Pyshkin S. New prospect for optoelectronics. Nanoscience & Technology 2016; 3(1): 1-5.

[34] Pyshkin SL. Excitonic crystal and perfect semiconductors for optoelectronics. Chapter 1. In: Materials and Devices. SL Pyshkin and J Ballato, editors, Rijeka: InTech; 2015; 1-30.

[35] Shanmin G, Jun L, Nan C, Yan Z, Yi X. Aqueous synthesis of III-V semiconductor GaP and InP exhibiting pronounced quantum confinement. Chemical Communications 2002: 3064-5.

[36] Zhengang L, Yujun B, Deliang C, Qilong W. Preliminary insight into the formation process of InP and GaP nanocrystals. Solid State Sciences 2003; 5: 1037-40.

[37] Zhang Z-C, Wang B-P. Diamond and oxidized disordered graphite on the surface of gallium phosphide nanoparticles. Systems Characterization 2009; 26: 53-7.

[38] Paul W. Band structure of the intermetallic semiconductors from pressure experiments. Journal of Applied Physics 1961; 32: 2082-94.

[39] Zallen R, Paul W. Band structure of gallium phosphide from optical experiments at high pressure. Physical Review 1964; 134: A1628-41.

[40] Pyshkin SL, Fedoseev SA, Lagomarsino S, Giannini C. Preparation and structural properties of some III-V semiconductor films grown on (100) oriented Si substrates, Journal of Applied Surface Science, 1992; 56-58: 39-43.

[41] Budyanu VA, Chechuy SN, Pyshkin SL, et al. Investigation of III-V/Si heterojunction grown by laser deposition. Physica Status Solidi (a) 1985; 91: 737-44.

[42] Budyanu VA, Chechuy SN, Pyshkin SL, et al. Laser vacuum epitaxy of III-V semiconductors on silicon. Revue Roumaine de Physique 1987; 32(1-2): 216-19.

IntechOpen

IntechOpen