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# Long-Term Convergence of Bulk- and Nano-Crystal Properties

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## 1. Introduction

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 degradation in the performance of the associated devices.

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 an ordered redistribution of impurities and host atoms in a crystal. In the particular case of GaP, any attempt to accelerate these processes through annealing 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 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 (Pyshkin et al., 1990a). Hence, the observations of highly excited luminescence and some other phenomena in the crystals made in the 1960s-1970s and in the 1980s-1990s were then compared with the results obtained in 2009-2010 under similar experimental conditions.

The pure and doped GaP crystals discussed herein were prepared about 50 years ago (Goryunova et al., 1969). Throughout the intervening decades they have been periodically re-evaluated in order to investigate the change over time in their electro- and photoluminescence (PL), photoconductivity, bound excitons of high density, 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.

The long-term ordering of doped GaP and other semiconductors has been observed as an important accompanying process, which can only be studied using the same unique set of samples and the interest to observe them over decade time scales. More specifically, since

2005, we have analyzed the optical and mechanical properties of single crystalline Si, III-V semiconductors {GaP (Goryunova et al., 1969)}, and their ternary analog CdIn<sub>2</sub>S<sub>4</sub> (Pyshkin et al., 1990b), 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 (Goryunova et al., 1969; Ashkinadze et al., 1968; Pyshkin & Zifudin, 1974; Pyshkin, 1975a; Pyshkin et al., 1990a,b; Pyshkin et al., 1993; Pyshkin & Anedda, 1993, 1998), and during 2000s (Pyshkin, 2002a,b; Pyshkin & Ballato, 2005, 2006, 2008, 2010; Pyshkin et al., 2006, 2007a,b,c, 2008, 2009a,b,c,d,e, 2010a,b,c,d; Pyshkin, 2009-2012) along with those of newly made GaP nanocrystals (Pyshkin et al., 2006, 2010b,c; Pyshkin & Ballato, 2010); and freshly prepared bulk single crystals (Pyshkin et al., 2009a,b,c,d,e).

Jointly with the above-noted references this chapter provides a generalization of the results on long-term observation of luminescence, absorption, Raman light scattering, and microhardness of the bulk single crystals in comparison with the same properties of “modern” 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 prolonged room-temperature thermal annealing, and the interesting optical properties that accompany such ordering. We demonstrate that long-term natural stimuli that improve the perfection of crystals prevail over other processes, which could lead to novel heterogeneous systems and new semiconductor devices with high temporal stability.

Additionally, it is worth noting, that semiconductor nanoparticles for optoelectronic applications also were synthesized mainly to avoid limitations inherent to freshly grown bulk semiconductors with a wide range of different defects. For instance, different defects of high concentration in freshly prepared GaP single crystals completely suppress any luminescence at room temperature due to the negligible 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 equivalent to the best nanoparticles and stimulated emission with pronounced quantum confinement effect. These perfect crystals, due to their unique mechanical and optical properties, are useful for application in high-quality optoelectronic devices as well as they are a new object for development of fundamentals of solid state physics and, nanotechnology and crystal growth.

Lastly, for completeness, during the recent years, since 2005, the authors have continued their efforts on the preparation of GaP nanoparticles in order to improve their quality and to apply their composites with appropriate polymers for advanced light emissive structures (Pyshkin et al., 2006, 2010c, d; Pyshkin & Ballato, 2010; Pyshkin, 2009-2012). Application of the GaP/polymers nanocomposites in device structures for accumulation, conversion and transport of light energy have only recently received attention while bulk and thin GaP films have been successfully commercialized for many years.

## 2. Results and discussion

The discussion of results begins with the synthesis of GaP nanoparticles and nanocomposites such that a comparison can then be made to the properties of bulk single crystals.

## 2.1 GaP nanocrystals and nanocomposites: improvement of quality and properties

### 2.1.1 Nanocrystals

The highest quality GaP nanoparticles have been synthesized using white phosphorus under mild aqueous low temperature conditions. The photoluminescence (PL) and Raman light scattering (RLS) spectra, X-ray diffraction (XRD) and electron microscopy (TEM) of the nanoparticles prepared under different conditions have been compared with each other as well as with those from bulk single crystals. After the relevant investigation of different regimes and components for hydrothermal reactions this type of the synthesis has been chosen as an optimal (Pyshkin et al., 2010b); the other advanced methods are also under elaboration (Pyshkin, 2009-2012).

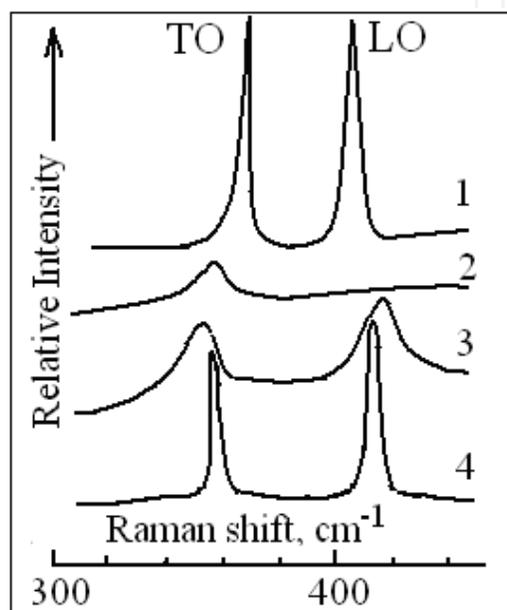


Fig. 1. Raman light scattering from GaP nanoparticles of different treatment (spectra 2-4) and in comparison with perfect GaP bulk crystals (spectrum 1). 2. Not thoroughly treated powder of nanoparticles prepared using red phosphorus at 200°C. 3. Thoroughly treated GaP nanoparticles prepared using red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

Note that according to our investigations of the conditions of the synthesis and data on nanoparticle characterization (TEM, XRD, RLS and PL), only a combination of low temperature synthesis, using white P and thorough ultrasound treatment of the reaction products during the synthesis and after leads to the creation of nanoparticles suitable for high quality light emissive nanocomposites (Pyshkin et al., 2010c) with the controlled broad-band and UV shift of luminescence. Further, the use of an ultracentrifuge to separate the nanoparticles based on their dimension provides an opportunity to efficiently change the line-width and spectral position of the luminescent maximum. The suspensions, specially produced for storage of the nanoparticles and preparation of nanocomposites, contain 10 nm single nanoparticles obtained from thoroughly ultrasonicated and washed reaction product, while its powder consists of the particles with the dimensions up to 100 nm and their clusters.

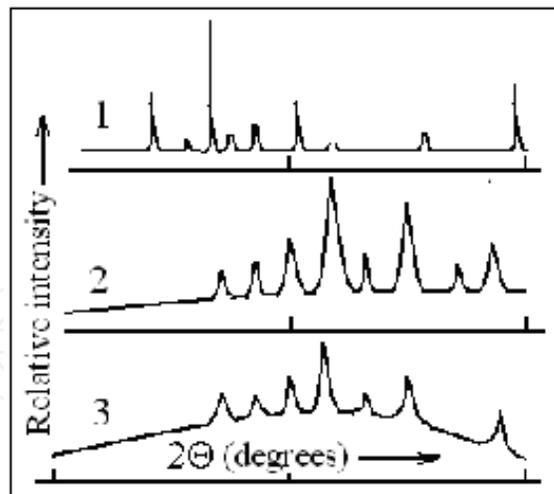


Fig. 2. X-ray diffraction from GaP nanoparticles. 1. White phosphorus, best performance of low temperature syntheses, well-treated powder. 2. White P, not the best performance and powder treatment. 3. Red phosphorus, the best result obtained using red P.

**Figure 1** shows the Raman light scattering spectra from the GaP perfect bulk crystals (**spectrum 1**) and from the nanoparticles prepared using either white or red P by mild aqueous synthesis at increased or low temperatures and ultrasonically treated (**spectra 2-4**). The characteristic Raman lines from the nanoparticles prepared at high temperatures (**spectra 2 and 3**), especially from not thoroughly washed powder (**spectrum 2**), were weak and broad, while the lines from the nanoparticles prepared at low temperature using white P were narrow and intense (**spectrum 1**).

**Figure 2, spectra 1-3**, provides the X-ray diffraction spectra from GaP nanoparticles prepared at different conditions using red or white phosphorus. The nanoparticles obtained by low temperature aqueous synthesis using white phosphorus develop clear and narrow characteristic lines (**spectrum 1**) similar to those obtained of bulk GaP taken from our long-term (more than 40 years) ordered GaP single crystals (Pyshkin et al., 2010b).

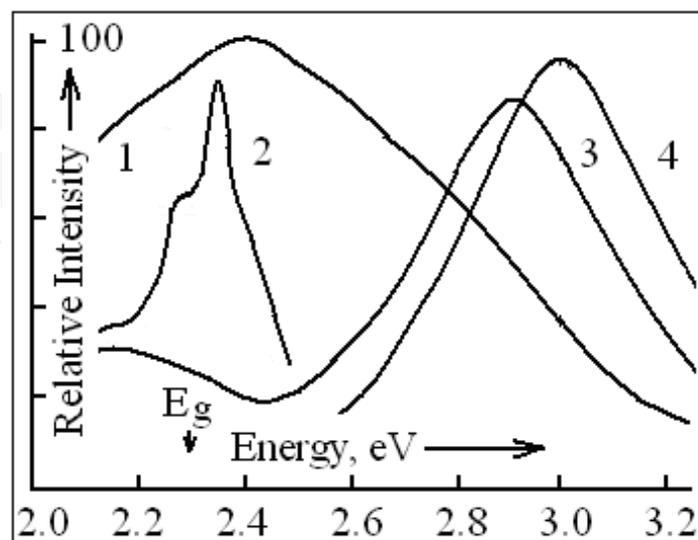


Fig. 3. Luminescence spectra from perfect, long-term ordered GaP single crystals (1) in comparison with the spectra of GaP nanoparticles, prepared in 2005 (2) and now (3, 4).

Initial results on the luminescent properties of GaP nanoparticles (Pyshkin et al., 2006) confirm the synthesis of 10 nm GaP nanoparticles with clear quantum confinement effects. The luminescent spectrum was not bright enough and its maximum was only slightly blue shifted against the 2.24 eV forbidden gap at room temperature (**Fig. 3, spectrum 2**). The nanoparticles obtained from the reaction with white P at low (125 °C) temperature exhibit an intense broad-band spectra considerably blue-shifted (**Fig. 3, 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 large particles with the maximum close to the edge of the forbidden gap in GaP (**Fig. 3, spectrum 3**). A thorough ultrasonic treatment yields a more pure fraction of nanoparticles, shown the **spectrum 4**, having the maximum at 3 eV and no maximum in the vicinity of the GaP forbidden gap.

It is reasonable to use such particles in GaP nanocomposites given the goal to obtain broad band luminescence from UV to the yellow-red region with controlled spectral width and position of maximum.

Thus, it was established that GaP nanoparticles can be prepared from white phosphorus at decreased temperature (125°C), intense ultrasonication during the syntheses and, if necessary, separation based on size using ultracentrifuge. These optimal conditions for GaP nanoparticles syntheses have been chosen in our works on fabrication of the GaP/polymers nanocomposites. The other possibilities to get the nanoparticles of the best quality are discussed in (Pyshkin et al., 2011).

### 2.1.2 GaP/Polymers nanocomposites

In the preparation of the nanocomposites, the fractions of uniform GaP nanoparticles were used following thorough ultrasonic treatment and a number of other operations that yielded the bright broad-band luminescence from UV until yellow-red region with controlled width and position of maximum. It is important to note that the value of the forbidden gap in GaP at room temperature is only 2.24 eV and its bulk freshly prepared single crystals have no luminescence at 300 °K.

Different polymers [Polyglycidyl methacrylate (PGMA), polyglycidyl methacrylate-co-polyoligoethyleneglycol methacrylate (PGMA-co-POEGMA) and biphenyl vinyl ether (BPVE)], compatible with GaP nanoparticles have been used in preparation of the nanocomposites. The details of their fabrication are described in (Pyshkin et al., 2010c).

The nanocomposite films were deposited from a suspension in water-ethanol mixture solution on the surface of a silica substrate via the procedure known as dip-coating. Surface morphology of the nanocomposite films was studied in ambient air by AFM in the tapping mode, on a Dimension 3100 (Digital Instruments, Inc.) microscope. Thickness of the polymer composite film was within 250-300 nm defined from AFM scratch experiment. Luminescence of the nanocomposites films was excited by the N<sub>2</sub> laser nanosecond pulses at wavelength 337 nm and measured at room temperature. AFM imaging demonstrated that no significant aggregation was caused by the polymerization. In general, individual particles were observed.

Thus, the thoroughly washed, ultrasonicated and dried nanopowder obtained by mild low temperature aqueous synthesis from white P may be used for fabrication of quite good blue light emissive nanocomposites (**Figure 4, spectrum 1**), but the best quality and the largest shift of the position of luminescence maximum to the UV side (up to 3, 2 eV) can be obtained only in the case of fabrication of the nanocomposite from similarly prepared

nanoparticles with the dimension of approximately 10 nm and stored as a suspension in a suitable liquid (Figure 4, spectrum 2).

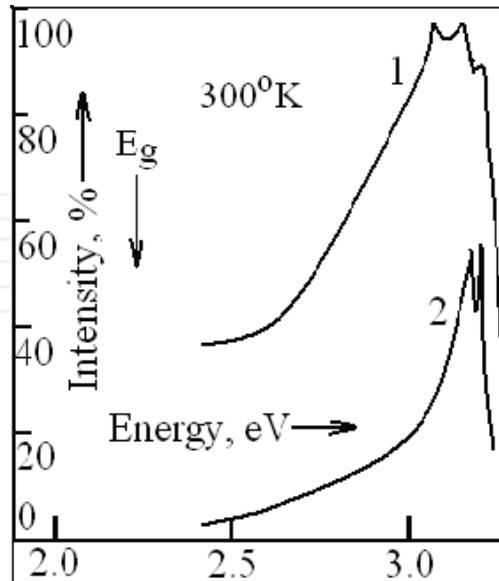


Fig. 4. Luminescence spectra of GaP/PGMA-co-POEGMA nanocomposite prepared on the best GaP nanoparticles synthesized and stored as the dry powder (spectrum 1) or suspension in a liquid (spectrum 2).

**Figure 5** shows the luminescence spectra of 2 nanocomposites produced on the base of 2 batches of GaP nanoparticles obtained under different conditions (temperature, modification of P, etc.). 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.

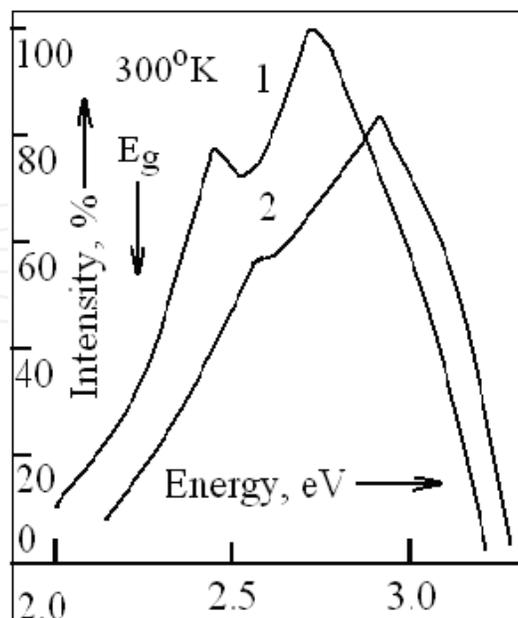


Fig. 5. Luminescence spectra of 2 GaP/BPVE nanocomposites produced on the base of 2 parties of GaP nanoparticles prepared using different conditions.

Initial attempts to prepare GaP nanoparticles, dating from the years 2005-2006 (Pyshkin et al. 2006), yield room temperature luminescence with maximum shifted only to 2.4 eV that in comparison with the new maximum at 3.2 eV confirms serious achievements in technology of GaP nanoparticles and GaP based nanocomposites.

## 2.2 Aged and freshly grown crystals: comparison of properties

We begin by comparing selected properties of pure and doped GaP crystals measured recently to those measured many years ago in order to better understand their luminescence behavior.

Luminescence and Raman light scattering spectra indicate that over a period of about 25 years the zero-phonon line of the exciton bound to nitrogen, A, and its phonon replica LO, TO are narrower in their line widths (**Figure 6**) and in comparison with freshly prepared single crystals. Further, the zero-phonon line A and its phonon replica of single N impurity-bound excitons in the aged crystals shift according to the existing theory (Allen, 1968) their spectral positions with concentration of N impurities. In comparison with ordered GaP:N, newly grown crystals exhibit broader luminescence line-widths when the nitrogen concentration increases. These findings indicate that a more ordered disposition of N impurities with equal spacing exists between them in the aged crystals.

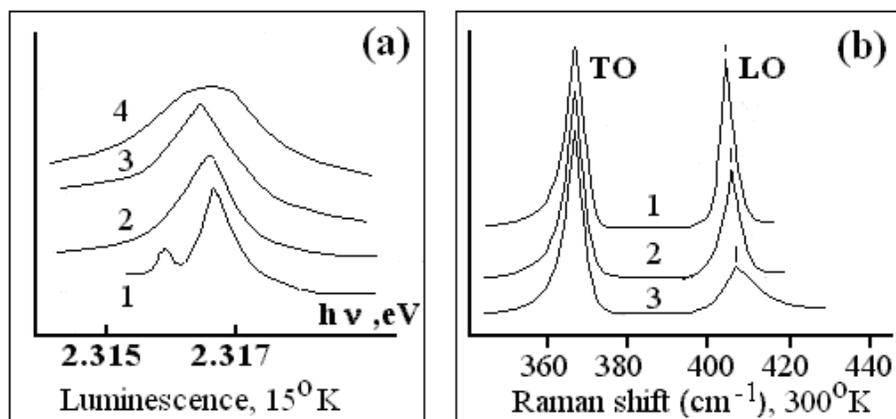


Fig. 6. Evolution of the non-phonon line of bound exciton A in luminescence (a), excitation by Ar<sup>+</sup>-laser at 488 nm, 15K) and its LO (longitudinal optical) and TO (transversal optical) phonon replica in Raman light scattering (b), Excitation by Ar<sup>+</sup>-laser at 514 nm, 300K) as a function of N (nitrogen) concentration. 1-3: ordered crystals. 4: unordered. 1-4:  $N_0 = 10^{17}$ ;  $10^{18}$ ;  $10^{19}$  and  $10^{18} \text{ cm}^{-3}$ .

**Figure 7** shows the Raman spectra of pure GaP and GaP:N in 1989–1993 (a) and in 2006 (b, c). It is observed that the line-width and position of transverse optical (TO) modes are largely the same now as in 1989–1993 and do not depend on impurity concentration. In the case of the longitudinal optical (LO) modes, the peaks from the original sample are broad and weak and shift with impurity level. After 40 years, these peaks are now much more intense, possess narrower linewidths and have a spectral position that no longer depends on N concentration. In earlier measurements, the intensity of the LO peak was only a few times less in heavily doped than in the pure disordered crystals. Now the same crystals display a reversal in the ratio between the intensities of these peaks.

A new phenomenon observed in the Raman spectra, that has developed in the crystals over 40 years, are the peaks denoted by us here as LA, 2TO and TO + LO (**Figure 7c**). Note that the

theory of Raman light scattering in GaP predicts the LO phonon to decay into two longitudinal acoustic (LA) phonons. LA phonons with a frequency  $LO/2$  (Bairamov et al., 1975), and two-phonon processes of  $2TO$  and  $TO + LO$  emission can also be observed in perfect crystals (Pyshkin et al., 1990b). This observation of a multi-phonon process and a decay of LO phonon, having a low intensity, confirms the high quality of the host lattice, uniform impurity distribution, and as a consequence, low noise background in the Raman scattering.

**Figures 6-8** demonstrate differences between the disordered, newly prepared single crystals, and crystals ordered for 25 years and 40 years. As can be seen from Fig. 7, differences between the freshly prepared and 25-year ordered GaP crystals are observed in the line-widths and their spectral position with N concentration, which suggests an improvement in ordering of the host lattice and nearly equal spacing between impurities.

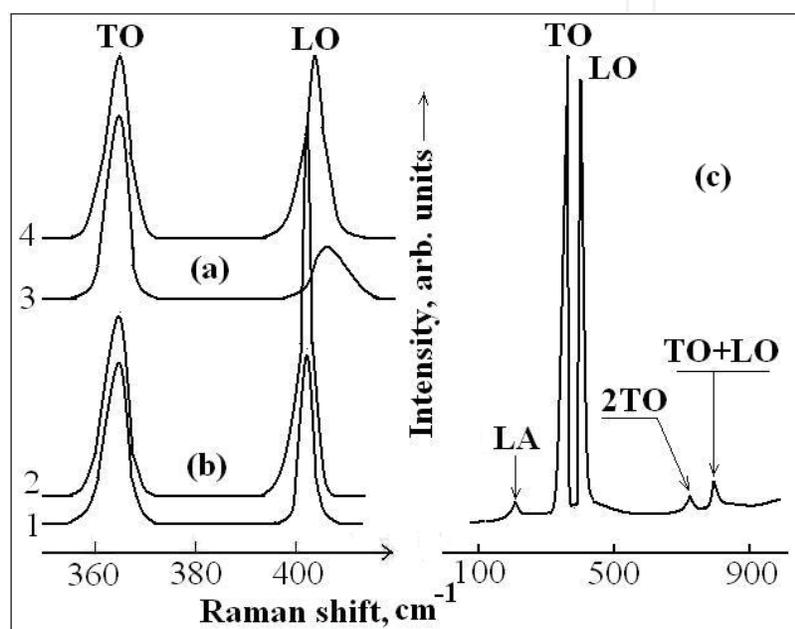


Fig. 7. Raman spectra in GaP and GaP:N in 1989-1993 (a) and in 2006 (b, c). 1, 4 - pure GaP, 2, 3 - GaP heavy doped by N.

**Figure 8** shows the absorption edge as a function of photon energy (a) and provides a comparison of microhardness and density of dislocations as a function of N concentration (b). The position of the absorption edge in freshly prepared GaP:N crystals does not depend on N impurity concentration and it coincides with the position for pure GaP crystals (**Figure 10a, curves 2 and 3**). This N impurity creates the 21-meV energy level under the conduction band for bound excitons both in freshly prepared and 25-year ordered crystals. On the contrary, curve 1, **Figure 8a**, shows that the GaP:N crystals ordered for approximately 40 years demonstrate an increase in the forbidden gap and the clear shift of the absorption edge, which is proportional to the N concentration according to Vegard's law, similar to that in a dilute GaP-GaN solid solution.

Let us discuss now the influence of long-term ordering of the dopants and defects on the optical and mechanical properties of GaP and its ternary analog  $CdIn_2S_4$ . The microhardness and dislocation density in these samples have been evaluated over many decades (Goriunova, 1960; Radautsan et al., 1969; Pushkash et al., 1978; Valkovskaya et al., 1984; Pyshkin, 1967). Taking into account the full 50-year timeframe makes an exact comparison difficult; therefore, only general trends are discussed here.

According to the classical point of view (Kittel, 1978), good plasticity is determined by free movement of dislocations through the crystal under mechanical loading. Impurities act to pin the movement of dislocations. Therefore, the value of microhardness,  $H$ , in GaP should depend on the impurity concentration (Fig. 8b, lines 1 and 2). As can be seen, the relatively pure crystals have minimum microhardness. An increase in the impurity concentration in GaP crystals, with the dopants such as N, Bi, simultaneously N and Sm (Pyshkin et al., 1990a; Pyshkin, 1967), substituting for the host atoms (N, Bi) or occupying the interstitials in the crystal lattice (Sm), leads to an increase in microhardness for the long-term-ordered crystals. The same behavior of microhardness for freshly prepared and long-term ordered single crystals was observed for mono-atomic Si and binary InP, pure and doped by different impurities.

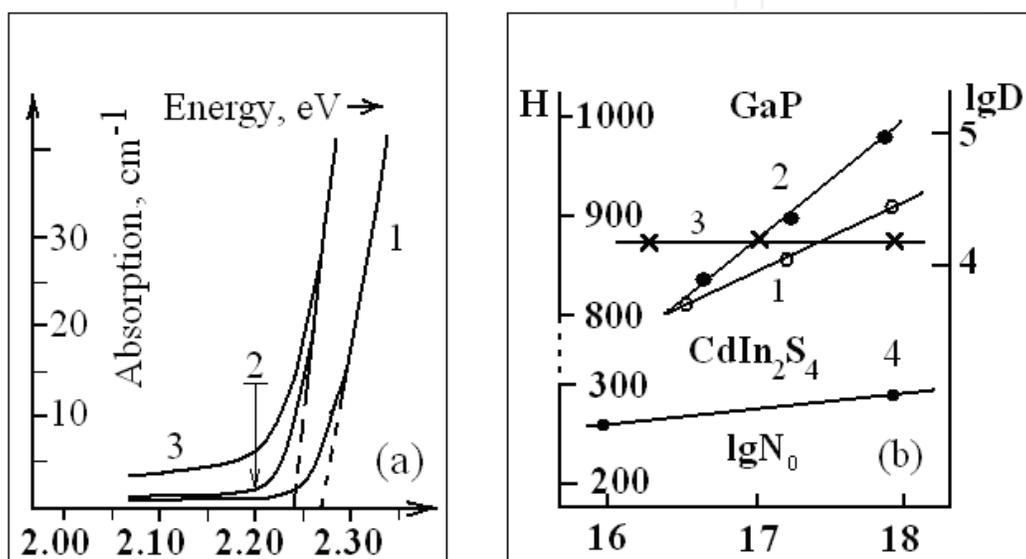


Fig. 8. (a) Absorption coefficient in long-term ordered (40 years) GaP:N (1) and in 25 years old (2) or freshly prepared undoped GaP (3). N concentration is  $10^{18} \text{ cm}^{-3}$ .

(b) Microhardness,  $H$ , in fresh unordered GaP crystals as a function of N concentration (1); the same for 40 years ordered crystals (2);  $D$  as a function of N concentration (3);  $H$  in CdIn<sub>2</sub>S<sub>4</sub> at different concentration of defects (4).

The rather large difference in microhardness of the long-term-ordered highly doped crystal relative to the newly grown crystals can possibly be explained by the regular disposition of impurities. This might create a more significant obstacle to dislocation movement than in the newly grown system, in which the impurities form clusters with large distances between them, permitting greater dislocation movement.

Figure 8b, line 3 shows that the density of dislocations  $D$  in GaP does not depend on time (at least over nearly 50 years), concentration of impurities, or the nature of their distribution along the crystal. It is possible that the method of crystal growth determines the density of dislocations. It is worth noting that the high-quality growth conditions for the initial GaP crystals and accurate control over temperature during growth considerably decreased the density of dislocations (Pyshkin, 1967).

As we have shown earlier (Pyshkin, 1971), optical properties and quality of crystal lattice of CdIn<sub>2</sub>S<sub>4</sub> highly depend on position and concentration of intrinsic structural (stoichiometric vacancies of In and Cd cations) and antistructural (In<sub>Cd</sub> and Cd<sub>In</sub> - In replaces Cd and vice versa in partly inverse spinel) defects. CdIn<sub>2</sub>S<sub>4</sub> due to wrong positions of cations has partly

inverse spinel structure instead of normal spinel and antistructural defect ( $\text{In}_{\text{Cd}}$ ,  $\text{Cd}_{\text{In}}$ ) concentration dependently on the growth condition up to  $10^{20} \text{ cm}^{-3}$  (Guzzi & Grilli, 1984). Analysis both of luminescence and Raman light scattering spectra (Pyshkin et al., 1990a; Pyshkin, 1971) shows that due to the long-term ordering the partly inverse spinel  $\text{T}_d^2$  turns into the normal spinel structure  $\text{O}_h^7$ . This implies that the high concentration of the antistructural defects characterizing freshly grown crystals will decrease from app.  $10^{20} \text{ cm}^{-3}$  until their equilibrium level of the order of  $10^{16} \text{ cm}^{-3}$ . As in GaP, where the microhardness highly depends on the concentration of impurities, its ternary analog demonstrates the considerable dependence of microhardness on concentration of the defects (**Figure 8b, the line 4**).

**Figure 9a** shows that the freshly prepared and then slowly cooled as well as the long-term ordered crystals having a small concentration of the antistructural defects, in comparison to quickly cooled crystals, develop fine structure of the luminescence due to interaction of electrons only with lattice phonons.

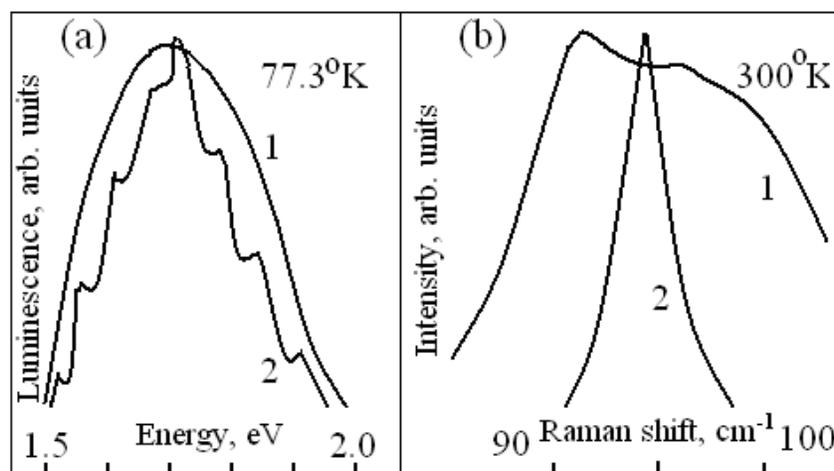


Fig. 9. Luminescence and Raman light scattering in  $\text{CdIn}_2\text{S}_4$ . (a) Luminescence of freshly prepared and long-term ordered  $\text{CdIn}_2\text{S}_4$  crystals. Rapid (1) and slow (2), less than  $5^\circ\text{C}$  per hour, cooling rates. Ordered crystals develop a spectrum like 2. (b) Raman light scattering at  $92 \text{ cm}^{-1}$  of unordered (1) and ordered (2) crystals.

Exactly as in GaP, a phonon mode is broad and weak for freshly prepared  $\text{CdIn}_2\text{S}_4$ , but after the long-term ordering this peak is more intense, has a more symmetric shape and narrower linewidth, characterizing harmonic vibrations in a perfect lattice (**Figure 9b, curves 1 and 2**). Now luminescence phenomena that can be observed only in perfect long-term ordered GaP and  $\text{CdIn}_2\text{S}_4$  single crystals will be discussed.

The 40-year ordered GaP:N crystals have no discrete impurity level in the forbidden gap and demonstrate uniform luminescence from a broad excitonic band (**Figure 10b**) instead of narrow zero-phonon line and its phonon replica in disordered and partly ordered (25-year-old, **Figure 10a**) single crystals. For the first time, to the best of our knowledge, the transformation of a discrete level inside the forbidden gap into an excitonic band (**Figures 10b and 11b**) is observed. In this case the impurity atom of nitrogen regularly is located into host lattice instead of phosphorus and affects the band structure of the crystals, which is now a dilute solid solution of GaP-GaN but not GaP doped by occasionally located N atoms. Note that the increase in the level of excitation of luminescence (**dotted lines in Figure 10**) in the case of partly ordered GaP:N leads to a broad luminescence band as a result of bound

exciton interaction (Pyshkin & Zifudin, 1974), while in the case of perfectly ordered crystals one can see an abrupt narrowing of the luminescence band, probably due to stimulated emission in perfect non-defect crystals as is discussed further below.

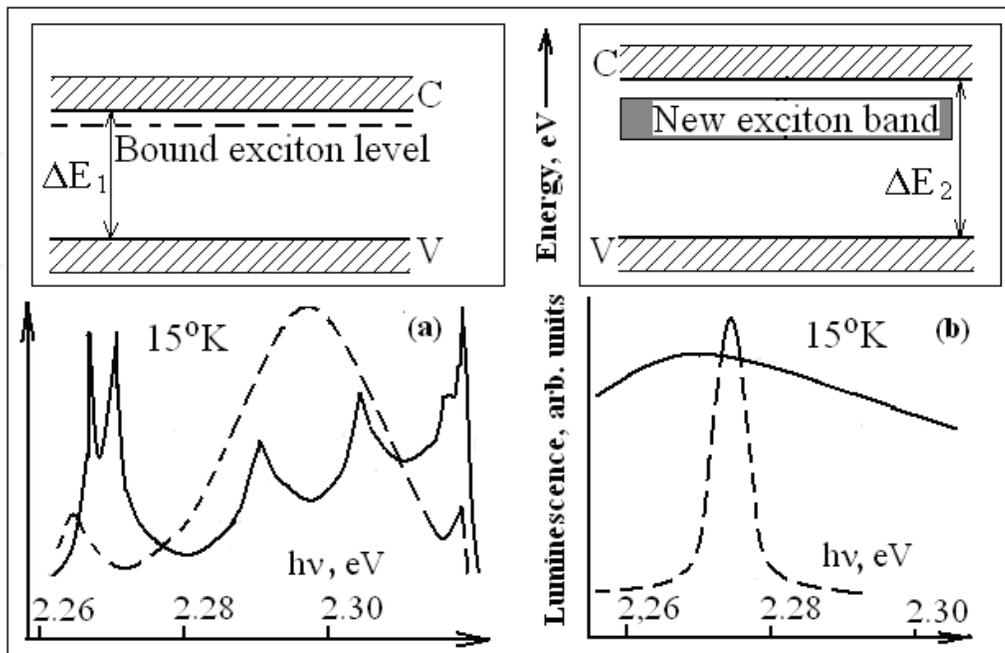


Fig. 10. Luminescent spectra and the view of the forbidden gaps ( $\Delta E_1$ ,  $\Delta E_2$ ) in the partly 25 years ordered (a) and perfect 40 years ordered (b) crystals GaP doped by N. The dotted lines correspond to highly optically excited crystals. C and V - the positions of the bottom of the conductance and the top of valence bands respectively.

Thus, 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 GaP doped by N (**Figure 11**) can be suggested. At relevant concentrations of N, the anion sublattice can be represented as a row of anions where N substitutes for P atoms with the period equal to the Bohr dimension of bound exciton in GaP (approximately 10 nm) (**Figure 11a**). At some level of excitation, all the N sites will be filled by excitons, creating an excitonic crystal (**Figure 11b**) which is a new phenomenon in solid-state physics and a very interesting model for application in optoelectronics and nonlinear optics (Pyshkin et al., 2008).

This new crystal lattice in which the impurities have become its intrinsic component can be corroborated by recent Raman light scattering experiments. The difference in the present ordered state of the crystal lattice, with respect to the data obtained with the same crystals and conditions during 1989–1993 (Pyshkin et al., 1993; Pyshkin, 2002) can be seen in **Figures 7a and b**, which shows the Raman spectra of pure GaP and GaP:N (Pyshkin et al., 2007, 2008). One can see (**Figure 7a, curves 3 and 4**) that, for the longitudinal optical (LO) phonon modes, the peak from the original samples is broad, weak, and shifts with impurity level. After 40 years (**Figure 7a, curves 1 and 2**), this peak is much more intense, has a symmetric (Lorentzian) shape, narrower linewidth, and a spectral position that no longer depends on N concentration.

These results are characteristic of harmonic vibrations in a perfect lattice. The LO phonon line is narrower in the doped crystal (**Figure 7a, curve 2**) than in the undoped (pure) crystals (**Figure 7a, curve 1**) and also is more intense than the TO phonon line. The same results have

been obtained for various impurities (N, Sm, and Bi) in spite of their maximum possible concentrations in GaP and different masses of impurity atoms and different types of substitution (N and Bi impurities substitute P sites in the crystal lattice whereas Sm occupies interstitials) (Pyshkin et al., 2007). These results confirm the important role of the impurities that are periodically located in the host crystal lattice and result in the formation of the new perfect crystal lattice.

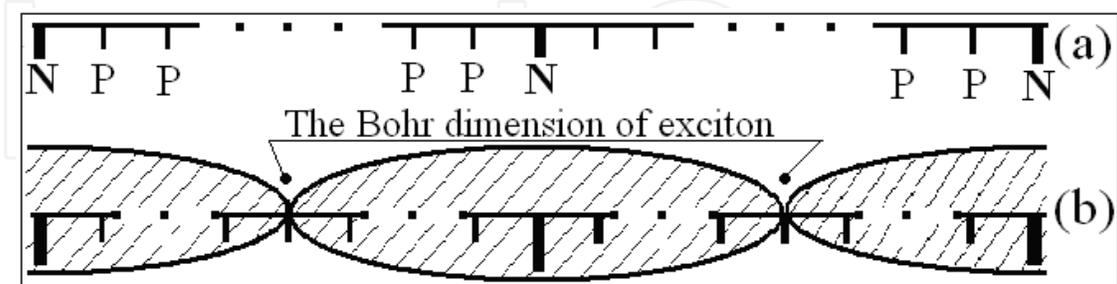


Fig. 11. The models of 40 years ordered GaP doped by N. (a) The new type of crystal lattice where the host P atoms are periodically substituted by N atoms. (b) The exciton crystal on the base of this crystal lattice. The substitution period is equal to the Bohr dimension of exciton (app. 10 nm) and the optical excitation should be sufficient to fill the N sublattice.

As noted previously (Pyshkin et al., 2008), due to a large concentration of defects and a large nonradiative recombination rate for non-equilibrium current carriers, the luminescence of fresh doped and undoped crystals only could be observed at temperatures below 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 40 years, luminescence of the long-term-ordered bulk crystals similar to the GaP nanocrystals (Pyshkin et al., 2008, 2010c, d,) clearly is detected in the region from 2.0 eV to 3.0 eV at room temperature. We suppose that, 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) high efficiency of so called "hot" luminescence in perfect crystals.

Thirty-five years ago, laser action had been observed only in highly optically excited, high-quality-factor resonators of GaP and at temperatures of 80 K and below. Taken from (Pyshkin, 1975b), **Figure 12** demonstrates that the stimulated emission can be observed only if the excitation light band is located perpendicular to resonator planes (**Figure 12a**). The stimulated emission takes place in the case presented in **Figure 12a** only since this geometry supplies the necessary condition when light losses are less than amplification in the resonator.

The stimulated emission previously observed only at 80 K and below (**Figure 12a**) is due to the radiative recombination of bound excitons that are accompanied by LO phonon emission.

The bright broadband luminescence is observed at room temperature from the long-term-ordered single crystals. In **Figure 13**, the stimulated emission is developed at 300°K and indirect optical transition by radiative 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.

The fact that the bright luminescence is seen at photon energies exceeding the energy gap confirms the high degree of perfection of the crystal. Additionally, this "hot" luminescence provides a good opportunity for fabrication and application of interesting light emissive device structures.

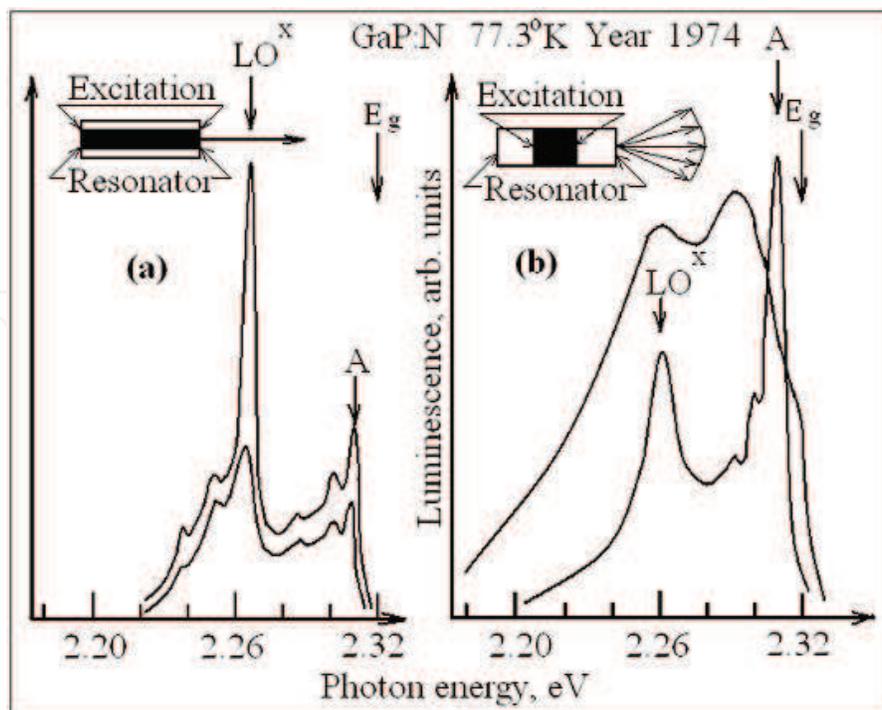


Fig. 12. Year 1974. Emission spectra of GaP excited by the 2nd harmonic of a Q-switched Nd<sup>+</sup> laser at different relation between losses and amplification of the emitted light. (a) Excitation light is perpendicular to the resonator planes, amplification exceeds losses. (b) Excitation light is parallel to the resonator planes, losses exceeds amplification.

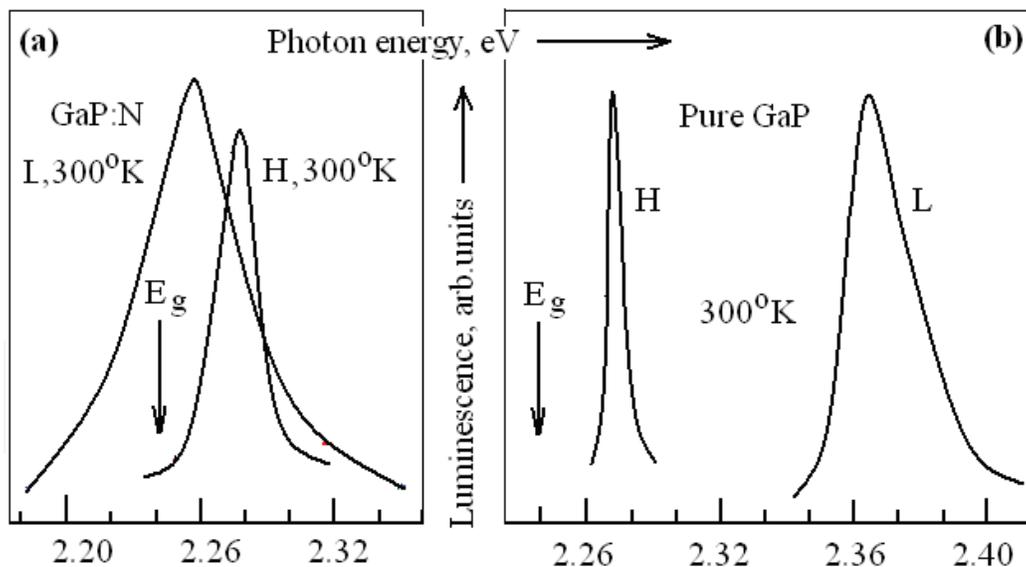


Fig. 13. Year 2007. 300K. Emission spectra of N doped (a) and pure (b) GaP grown in 1965. The letters L and H at the luminescent curves mean low and high level of excitation respectively.

**2.3 Comparison of properties of nanocrystals, aged and freshly-grown bulk crystals**

The high quality of our long-term ordered semiconductor crystals as well as the considerable improvement of their mechanical and optical properties in comparison with

the same freshly-grown crystals are confirmed by investigations of luminescence, light absorption, Raman light scattering, X-ray diffraction, microhardness and discussed in a number of papers and presentations (Pyshkin & Anedda, A., 1993, 1998; Pyshkin, 2002; Pyshkin & Ballato, 2005, 2006, 2008, 2010; Pyshkin et al., 1990, 1993, 2006-2011). The most convincingly this statement can be illustrated by the comparison of luminescence from GaP bulk and nanocrystals.

**Figure 14** presents luminescence spectra of our long-term (up to 50 years) ordered GaP single crystals (**spectrum 1**) in comparison with the spectra of GaP nanoparticles (and their nanocomposites), prepared under different conditions. As already noted, luminescence was absent at room temperature in newly-grown bulk single crystals, but the same crystals, aged app. 50 years, exhibit bright broad band luminescence at 300°K between 1.8 – 3.2 eV with the maximum blue-shifted from the position of the GaP forbidden gap ( $E_g = 2.24$  eV).

Nearly the same spectrum of luminescence is observed from nanocrystals provided that they are not separated on their dimension (**spectrum 2**). Nanocrystals of sizes close to 10 nm and stored as dry powder demonstrate rather broad luminescent band with maximum at 3 eV (**spectrum 3**). At last, nanocrystals of about 10 nm sizes, thoroughly separated and distributed in a suspension, that prevent their coagulation, mechanical and optical interaction, have bright narrow-band luminescence with maximum at 3.2 eV, approximately 1 eV far from the position of the absorption edge in GaP at 300°K (**Spectrum 4**).

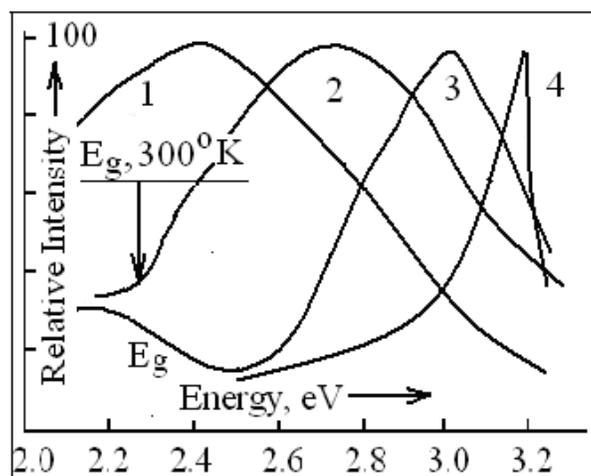


Fig. 14. Luminescence of perfect bulk GaP single crystals (1) in comparison with the luminescence of GaP nanoparticles (2-4). Nanoparticles have been prepared using white P by mild aqueous synthesis at decreased temperature and stored as the dry powders (spectrum 2, 3) or suspension in a liquid (spectrum 4). The other details are in the text.

Thus, perfect GaP bulk crystals as well as nanoparticles have no practical difference in their luminescence behavior, brightness or spectral position. This implies the negligibly small contribution of non-radiative electron-hole recombination and an opportunity for current carriers to move along the more perfect crystal lattice without any essential scattering on the defects inherent to freshly-grown single crystals.

### 3. Conclusion

This study of GaP:N and CdIn<sub>2</sub>S<sub>4</sub> 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 investigation the main trends of the evolution of optoelectronic and mechanical properties have been established. 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 observe 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. In GaP 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 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 should be a high priority.

This long-term evolution of the important properties 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 (Pyshkin, 1995, 1997; Pyshkin et al., 1996) will be applied to fabrication of device structures with artificial periodicity. Using these methods one can grow a multi-layer structure where the monolayer of N atoms will be incorporated in it each 10 nm, creating a one-dimensional periodic structure of N traps for excitons. Preparation of two dimensional perfect sublattice of N impurities along pure GaP film is rather difficult, but also is possible using ion lithography or atomic force microscope built into a growth chamber. Together with classic methods of crystal growth, these methods can be employed to realize impurity ordering that would yield new types of nanostructures and enhanced optoelectronic device performance.

It is worth noting in conclusion that semiconductor nanoparticles have been 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 discussed herein exhibit equivalent behavior to the best nanoparticles with pronounced quantum confinement effect. These perfect crystals are useful for application in high-quality optoelectronic devices as well as they are a new object for development of fundamentals of solid state physics.

#### 4. Acknowledgment

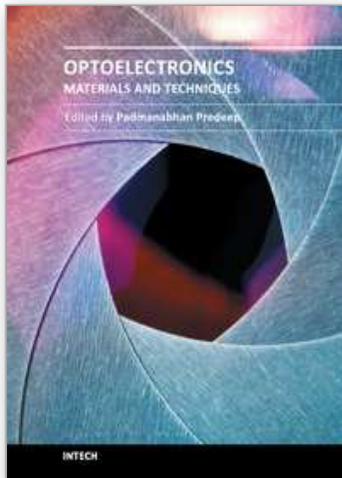
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