

# Luminescence of Long-Term Ordered Pure and Doped Gallium Phosphide

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Evolution of luminescence is reported from GaP crystals that were grown over 40 years ago. This is the longest running cycle of experiments to study the temporal effects of crystal lattice and impurity ordering. The results clearly indicate impurity ordering and the formation of a new type of crystal lattice in which periodically disposed impurities modify and improve properties of the crystal. A high-density exciton system bound to a nitrogen impurity superlattice and GaP:N, GaP:N:Sm nanocrystals distributed in transparent fluorine-containing polymers will be used as the base elements for a new generation of optoelectronic devices.

**Key words:** Luminescence, GaP, ordering, excitons, optoelectronics

## INTRODUCTION

In this study, we compare the luminescence from GaP crystals measured recently and years ago in order to investigate the evolution of the crystal lattice and the nature of impurity distribution. Now and then, we used the same GaP crystals grown by one of the authors (SLP) in 1963 to 1966, characterized for the first time in 1966 and 1968<sup>1,2</sup> and then presented at relevant conferences around the world.<sup>3–16</sup> Recently we published a similar comparison made on the base of Raman light scattering (RLS)<sup>10</sup> and the comparison of mechanical properties of the freshly prepared and long-term ordered crystals.<sup>11</sup> After approximately 15 years since these samples were last monitored<sup>4,5,12</sup> and more than 40 years since they were prepared,<sup>1</sup> this work as well as others<sup>8,9–11,13</sup> undertakes the next cycle of investigation of the long-time ordering of impurities in the GaP crystal lattice.

Gallium phosphide (GaP) has received significant attention as a material for use in a wide range of important modern optoelectronic devices including

photodetectors, light emitters, electroluminescent displays, and power diodes as well as being a model material with which to investigate the fundamental properties of semiconductors. In particular, GaP doped with nitrogen (GaP:N) offers a unique opportunity to study the high-density system of excitons bound to an ordered N-impurity superlattice.<sup>5,12,14</sup> In an analogous manner, GaP:Bi<sup>15</sup> and GaP:N:Sm<sup>16</sup> also have intriguing properties for use in photonic technologies. In the GaP:Bi system, excitons bound to Bi have nearly four times the binding energy of the N-bound excitons (approximately 0.02 eV) and so can persist at rather high temperatures. GaP:N:Sm is equally interesting because the recombination (N) and activation (Sm) centers are distributed in a way that creates in the indirect band structure of GaP a mechanism for light emission in the yellow-green spectral region with very high efficiency (approaching 100%). Although naturally occurring crystals (e.g., diamonds and gemstones) are often of better quality than laboratory-grown semiconductor crystals due to the large difference in growth velocity, there have been considerable improvements in the quality of semiconductors over the past 40 years. For example, in order to realize the theoretical luminescent

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efficiency of 100%, it is necessary to prepare a uniform mixture of recombination (N) and coactivation (Sm) centers. However, in freshly grown samples, the crystal lattice contains many intrinsic defects (dislocations, vacancies, nonthermodynamic positions of host atoms) and the dopants can take on a more random site distribution and even clusters, lessening any cooperative effects.

With specific regard to GaP:N impurities, it was shown previously<sup>5,12</sup> that 25 years of storage at room temperature and atmospheric pressure yields a rather regular distribution of impurities (i.e., a more equal spacing between impurities in the lattice). It is believed that the driving forces for impurity redistribution are the strains associated with lattice deformation in the vicinity of impurity clusters and gradients in the impurity concentration. In the case of GaP:Bi and GaP:N:Sm, taking into account that N or Bi impurities can be located only in anion sites and Sm only in interstitial sites of the GaP lattice, one can expect that the uniform impurity sublattice will have some degree of translational symmetry. If the N or Bi impurity concentration is chosen to yield the average period of this superlattice of approximately the Bohr diameter of an exciton bound to these impurities (approximately 10 nm), then at the appropriate level of optical excitation the impurity superlattice will be filled by excitons creating a dense crystal-like system. These systems are very interesting as materials for research and as a medium for the generation of nonlinear optical phenomena at a very low light intensity. Note that the dense excitonic system of bound excitons in ordered GaP crystals will be better ordered than the empty impurity superlattice due to the intense processes of Auger recombination of the excitons separated from each other by distances less than their Bohr dimension.<sup>12,14</sup>

The ordered excitonic phase gives new opportunities for the accumulation, conversion, and transport of light energy. It seems that the use of bound excitons in GaP single crystals with ordered disposition of nitrogen impurities (GaP:N) represents a novel approach to advancing the state of the art in optoelectronic and photonic devices. This is true especially in regards to the collective properties of high-density bound excitons as a huge capacitance accumulator of light energy.

Our results in technology and characterization of GaP nanoparticles<sup>9,13</sup> demonstrate good prospects for their application in light-emissive devices. It was possible to prepare particles with diameter less than that of bound excitons in GaP:N and realize the quantum confinement effect,<sup>17</sup> leading to a considerable shift of the characteristic luminescence maximum to the short-wavelength side. The luminescence is very intense at room temperature while the same freshly prepared crystals display it only at low temperatures. Note that we have also found an excellent host medium for light-active GaP nanoparticles: perfluorocyclobutane (PFCB) polyaryl

ethers, which represent a relatively new class of partially fluorinated polymers that combine the processability and durability of engineering thermoplastics with the optical, electrical, thermal, and extreme environmental resistant properties of traditional fluoroplastics.<sup>18</sup>

The chemistry and optical properties of GaP:N single crystals and nanocomposites are the focus of joint activity in the framework of our US/Moldova Program. For this project, we will apply the technology of nanoparticles and nanocomposites as well as artificial ordering of impurity disposition in doped GaP with the help of modern epitaxial technologies.<sup>9,13,19–21</sup>

Thus, the current joint project of our institutions will realize new types of emitters, converters, and accumulators of light on the basis of successful implementation of organic and semiconducting materials.

## EXPERIMENTAL PROCEDURE AND DISCUSSION

References 1 and 2 detail the original preparation of the doped and undoped GaP samples. The single crystals were grown in 1961 to 1966 from super-high-purity Ga and P components at temperatures that excluded contamination of the crystals in the growth process. Use of a special furnace with very high-accuracy automatic control of temperature designed by us led to high-quality crystals grown in laboratory conditions. The crystals were doped with various chemical elements in order to ultimately purify them (Zr), to introduce donors D (VI group: S, Se, Te), acceptors A (II group: Zn), centers of radiative D-A recombination (Zn-Te, Zn-O), deep traps (elements of Fe group: Fe, Ni, Co), electron or hole traps with giant cross-section centers of bound exciton creation (N and Bi), centers of radiative recombination screened from temperature and crystal-field influences (rare-earth elements Sm, Gd or La), as well as impurities to increase the quantum output of irradiation to 100% (Sm + N).

The measurements were taken at room temperature and in a cold finger configuration at a sample temperature of approximately 37 K. The excitation was provided by a laser system (Spectra-Physics, Mod. Quanta Ray), in which the third harmonic of a Q-switched Nd:YAG laser feeds an optical parametric oscillator (OPO). The OPO output is pulsed light tunable in the 400 to 2000 nm wavelength range, with a pulse duration of about 4 ns; the laser energy is about 50 mJ/pulse for a wavelength around 500 nm. For all of the investigated samples, the OPO was set to the 490 nm wavelength, corresponding to a photon energy of 2.53 eV. The energy of the pulse was reduced to avoid damage to the samples as well as to prevent nonlinear optical processes. The emitted fluorescence was focused on the entrance slit of an Acton Mod. Spectrapro 300 I (600 g/mm) monochromator.

In our recent investigations of the Raman spectra from these samples,<sup>10</sup> we obtained new data similar to those obtained in 1989 to 1993, which are very useful for understanding the evolution of luminescence with long-term ordering processes.

Earlier, it was shown that the system of high-density bound excitons can be considered to be a solid excitonic phase similar to an inverted alkali metal and consisting of a net negatively charged heavy nuclei (N atom + captured electron) that interacts with a free hole gas.<sup>14</sup> The formation of this phase was detected by specific changes in the characteristic luminescent spectra (Fig. 1a) as well as by *p*-type photoconductivity of highly optically excited GaP:N as compared to the *n*-type dark conductivity of these crystals (Fig. 1b).<sup>4,14,22</sup>

It was also demonstrated that, despite the random distribution of N impurities along P sites just after preparation of GaP:N crystals, disposition of the impurities in anion sites as well as the intense Auger recombination between the bound excitons at a short distance from one other (less than the Bohr radius) give some initial ordering in the solid excitonic phase.

In 1980, Combescot and A la Guillaume<sup>23</sup> made a theoretical generalization of the experimentally observed collective properties that was published in 1974 by Pyshkin and Zifudin.<sup>14</sup> The authors<sup>23</sup> have proved that there exist two successive phase separations for an electron-hole system in a semiconductor having isoelectronic impurities within a certain density range. One is between bound excitons and a hole plasma with electrons pinned on the impurities, and the other is between this hole plasma and the usual electron-hole plasma.

Thus, 25 years ago, a solid excitonic phase with some inclinations of ordering that is similar to an excitonic crystal had been predicted and discovered. In contrast to the high-density system of free

excitons admitting only a liquid phase that does not exist in solid state, the solid bound excitonic phase has heavy nuclei with small zero vibrations like a usual crystal with metallic bonds, with a rather high critical temperature required to destroy this new phase (21 meV) and a lifetime  $10^{-7}$  s that is sufficient to observe its creation.<sup>2</sup>

A new stage of experiments with the aged (grown in the mid 1960s) GaP:N crystals started in the end of the 1980s when the evolution of luminescent and Raman spectra in long-term ordered GaP and some of its ternary analogues were revealed.<sup>22,24,25</sup> It was shown that from the 1960s to the 1980s impurity redistribution due to the respective substitution reaction with an energetic barrier of 1.0 eV to 1.2 eV at room temperature and normal pressure led to regular disposition of N along the anion sites.

The zero-phonon line A and its phonon replica of single N impurity-bound excitons in the aged crystals shifted their positions with the concentration of N impurities according to:

$$E_{NN} = E_N - \beta r_{NN}^{-3}, \quad (1)$$

where  $E_N$  is the A line position at  $r_{NN} \rightarrow \infty$ ,  $E_{NN}$  is the same at some nonzero nitrogen concentration, and  $\beta = 13$  if  $E_N$  and  $E_{NN}$  are measured in eV and  $r_{NN}$  in Å.<sup>26</sup> Compared with the ordered GaP:N, the fresh crystals only demonstrate broadening of the lines when the nitrogen concentration increases. This also confirms the ordered disposition of impurities with equal spacing  $r_{NN}$  in the aged crystals (Fig. 2a).

All the details of luminescent spectra of N impurity-bound single excitons can be observed in the aged crystals more clearly than in the fresh ones.<sup>5,10</sup> The low background of the exciton lines, their small half-width, and the distinct position in the spectrum. Thus, the observed long-term ordering is also

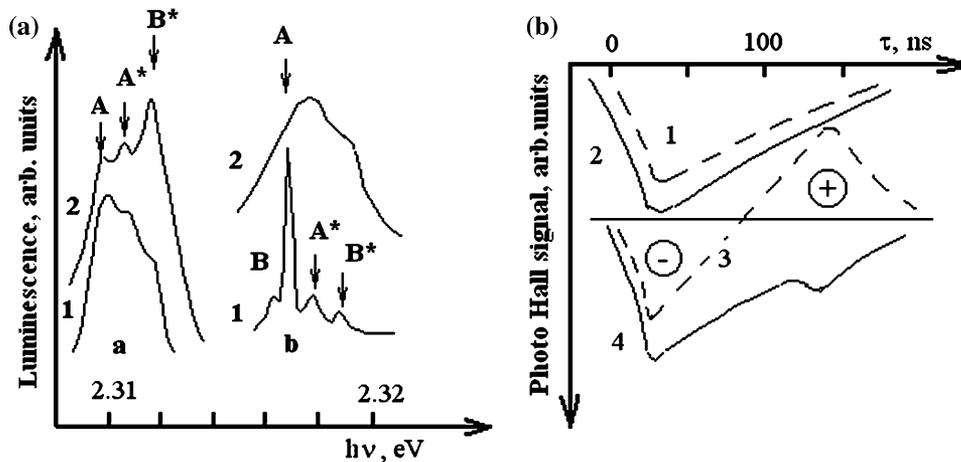


Fig. 1. Evolution of the luminescence, photoconductivity, and photo-Hall effect in GaP:N: (a) Evolution of GaP:N luminescent spectra at  $(n_1 \times a_1^3)^{1/3}$  less than unity (1) or equal to unity (2), where  $n_1$  and  $a_1$  are the exciton concentration and the Bohr radius, respectively. a: 4.2 K; b: 80 K; A, B: excitons; A\*, B\*: biexcitons; (b) Kinetics of photoconductivity (solid) and photo-Hall effect (dotted) in GaP:N, 80 K.  $(n_1 \times a_1^3)^{1/3}$  less than unity (1, 2) or equal to unity (3, 4).

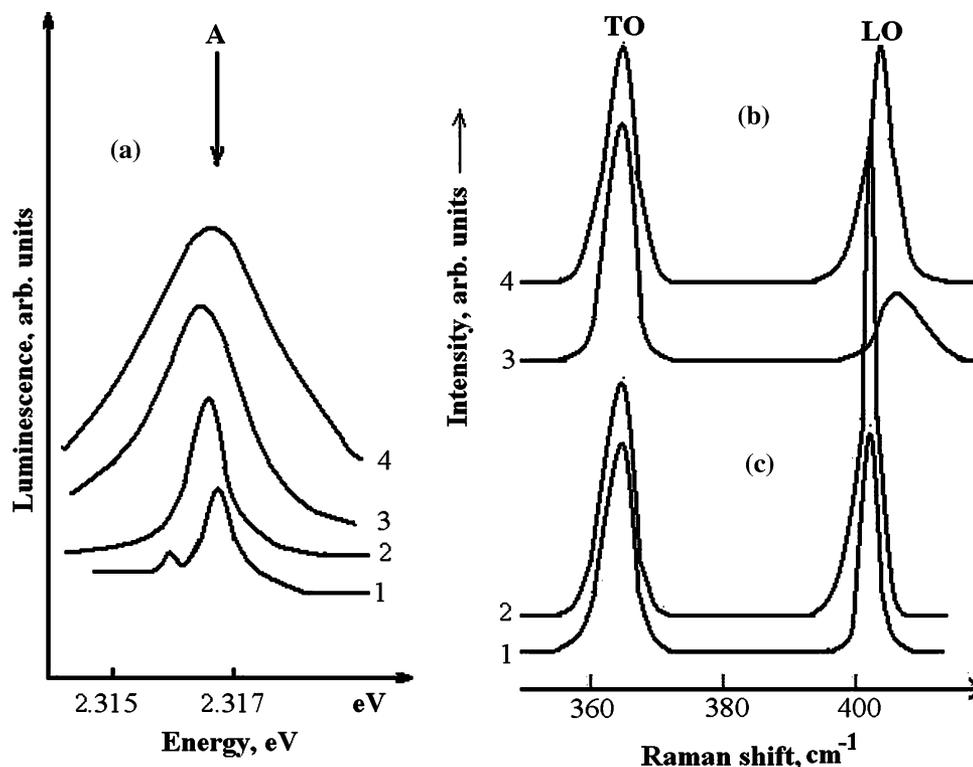


Fig. 2. Evolution of the zero-phonon line of bound excitons A as a function of N concentration (a) and Raman spectra of its phonon replica in GaP and GaP:N in 1989 to 1993 (b) and in 2006 (c). a: 15 K; 1–3: ordered crystals; 4: unordered; 1–4:  $N_0 = 10^{17} \text{ cm}^{-3}$ ,  $10^{18} \text{ cm}^{-3}$ ,  $10^{19} \text{ cm}^{-3}$ , and  $10^{18} \text{ cm}^{-3}$  concentration of N, respectively. b, c: 300 K; 1, 4: pure GaP; 2,3: GaP heavily doped by N. Spectra 3, 4 are taken from Ref. 5 and obtained by one of the authors (SLP) in 1991. TO, LO: transversal and longitudinal optic phonons, respectively.

true for the host constituents of the crystal lattice. In general, GaP:N crystals are considerably more perfect after 25 years than just after their growth. Note that we obtained nearly the same results for CdIn<sub>2</sub>S<sub>4</sub>,<sup>24,25</sup> the ternary analogue of GaP, which during this period turned from a partly inverse spinel structure  $T_d^2$  into the normal spinel  $O_h^7$ .

Other evidence for the ordered character of the impurity distribution is the shape of the zero-phonon line and its phonon replica: they are broad in newly prepared samples and narrower in long-term ordered crystals (see Ref. 10 and Fig. 1 therein). Furthermore, the intense lines associated with NN-pair excitons in the spectrum of the ordered crystals are absent because all the  $r_{NN}$  spacings at the level of the impurity concentration of  $10^{18} \text{ cm}^{-3}$  are equivalent and equal to  $\sim 10 \text{ nm}$ , while, for these NN pairs, the spacings range must extend from 0.345 nm ( $NN_1$ ) up to 1.219 nm ( $NN_{10}$ ).<sup>27</sup>

The difference in the present state of the crystal lattice of the same crystals in comparison with the data obtained in 1989 to 1993<sup>5,12</sup> can be seen in Fig. 2b, which shows the relevant Raman spectra of pure GaP and GaP:N.<sup>10</sup> While the line width and position of the transverse optical (TO) phonon modes are largely the same now and in 1989 to 1993 and do not depend on impurity concentration, in the case of the longitudinal optical (LO) phonon modes

the peaks from the original samples are broad, weak, and shift with the level of impurity concentration. After 40 years, these peaks are much more intense, have narrower line widths and a spectral position that no longer depends on N concentration. Now the same crystals display a reversal in the ratio between the intensities of these peaks.

Concerning the general differences in the spectra produced by the ordered and disordered forms of the crystals, note that in accordance with<sup>28</sup> the spectrum of the most ordered heavily N-doped crystal (spectrum 2 in Fig. 2b) shows a considerably more intense, narrow LO line than the less ordered pure or doped crystals (spectra 3 and 4 in Fig. 2b). Whereas the distribution and the environment of the P or N anions at a particular site of the unit cell in the ordered crystal are uniform, the variation in this environment from site to site exists in a disordered or less ordered crystal.

A new phenomenon observed in the Raman spectra, that has developed in the crystals over 40 years, is the new phonon peaks LA, 2TO, and TO + LO (see also, Ref. 10 and Fig. 2c therein) as the result of the decay of LO phonons<sup>29</sup> or the two-phonon emission in perfect crystals.<sup>24</sup> This observation of the multiphonon process and the 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.

One of the interesting results of the Raman light scattering obtained recently (2005 to 2006)<sup>10</sup> from pure and heavily doped GaP is the conclusion that the TO and LO phonon peaks maintain their spectral positions in pure and doped GaP crystals, independent of the type of impurity and its concentration (Fig. 2c). The LO phonon line is narrower in the doped crystal than in the undoped (pure) crystals and is also more intense than the TO phonon line. These results are obtained in spite of the maximum possible concentrations of N, Sm, and Bi in these crystals and the very different masses of N, Sm, and Bi impurity atoms, in the condition when the N and Bi impurities substitute P sites in the crystal lattice whereas Sm occupies interstitials.

Thus, it has been observed that, in long-term ordered highly doped GaP crystals, impurities do not distort the crystal lattice. This leads to the narrowing and increase of longitudinal optical-mode LO phonons and does not change the form and positions of the TO line.

The solid bound exciton phase is an absolutely new phenomenon. However, the previous results<sup>4,14</sup> only give arguments for its existence and now it is necessary to carry out a proper investigation of its properties such as crystal structure, luminescence, conductivity and charge transport, nonlinear effects, etc.

Continuing the monitoring of properties of our GaP single crystals grown 40 years ago,<sup>1</sup> in 2005 to 2006 we studied their luminescent properties in comparison with the data obtained in the 1960s, 1970s, 1980s, and 1990s,<sup>2-5,14-16,22</sup> as well as with the luminescence of GaP nanocrystals described in our earlier paper.<sup>9</sup> Here we discuss only some principal results; the details of this monitoring will be presented later on.<sup>30</sup>

Note that, due to the large concentration of defects and the intense nonradiative recombination of nonequilibrium current carriers, initially and for a long time,<sup>1,2</sup> the luminescence of fresh doped

and undoped crystals could be observed only at temperatures of 80 K and below. Then the luminescence band and lines were always seen at photon energies less than the value of the forbidden gap. Now luminescence of the long-term ordered bulk perfect crystals as for the aforementioned nanocrystals is clearly detected in the region from 2.0 eV to 3.0 eV at room temperature (see Fig. 3a,b, solid curves). The shape of the luminescence band and its maximum depend on the intensity of excitation. As before, the luminescence at 80 K (Fig. 3b, dotted curve) has the excitonic band maximum below the position of the forbidden band edge, but now a fraction of the luminescence spectra can be seen above the edge.

We suppose that in perfect 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 number of reasons. Among them are the very small concentration of defects and the relevant low contribution of non-irradiative electron-hole recombination, considerable improvement of crystal lattice, high transparency of perfect crystals, and low probability of phonon emission at indirect transition.

Figure 4a demonstrates luminescence through an indirect forbidden gap from pure long-term ordered perfect GaP single crystal at 300 K. The momentum conservation rule is fulfilled due to the participation of the lattice optical phonons. For the first time, the GaP:N:Sm crystals have been investigated when their luminescence could be observed only at 80 K and below.<sup>16</sup> The bright emission band arising in the presence of uniformly intermixed N recombination and Sm activation centers at 300 K is shown in Fig. 4b. Now the luminescence of the long-term ordered GaP:N:Sm at low temperatures develops very interesting properties, the details of which will be published elsewhere. Note that the long-term ordering gives a uniform mixture of Sm and N impurities and, according to Bell,<sup>31</sup> provides up to 100% quantum efficiency of radiation from the

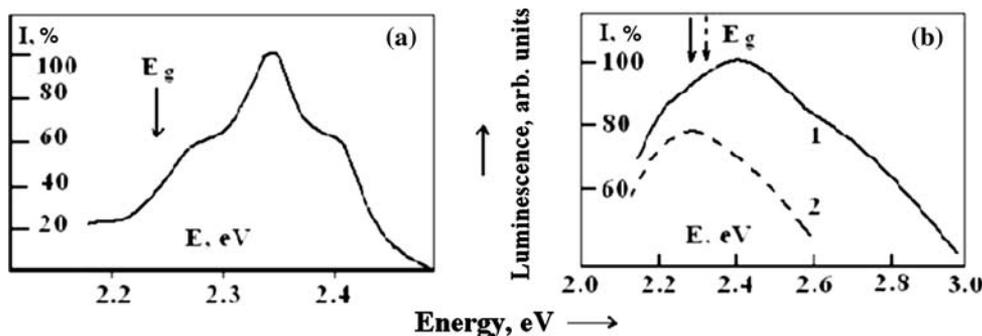


Fig. 3. Luminescence of nanoparticles and perfect bulk GaP. The position of the forbidden gap  $E_g$  at 300 K and 80 K is marked by arrows and the dotted arrow, respectively. (a) Luminescence of GaP nanoparticles with the dimensions of the order of 10 nm. Luminescence is observed at room temperature; compared with disordered bulk crystals its maximum is shifted to higher photon energies. (b) Luminescence of perfect bulk GaP single crystals prepared in 1966 and measured in 2006. Luminescence is observed at room temperature (curve 1) and its maximum is shifted to high energies of photons. Curve 2: 80 K.

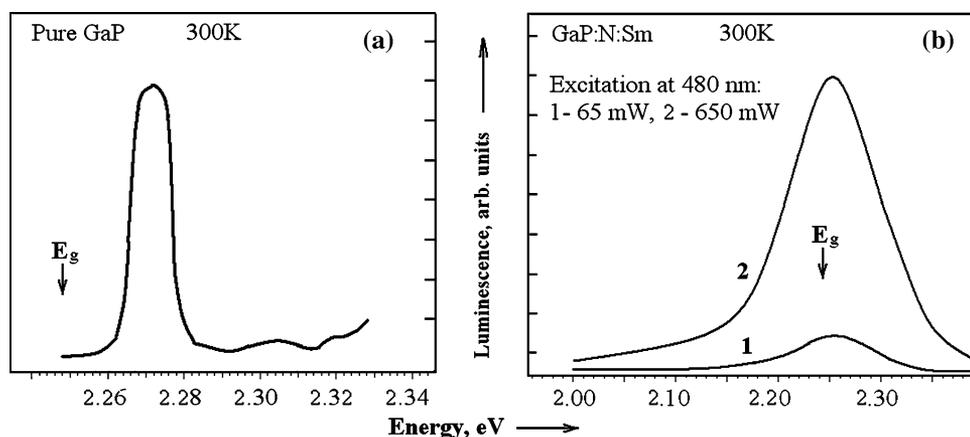


Fig. 4. Luminescence of the ordered pure (a) and doped by N:Sm (b) GaP crystals at 300 K.

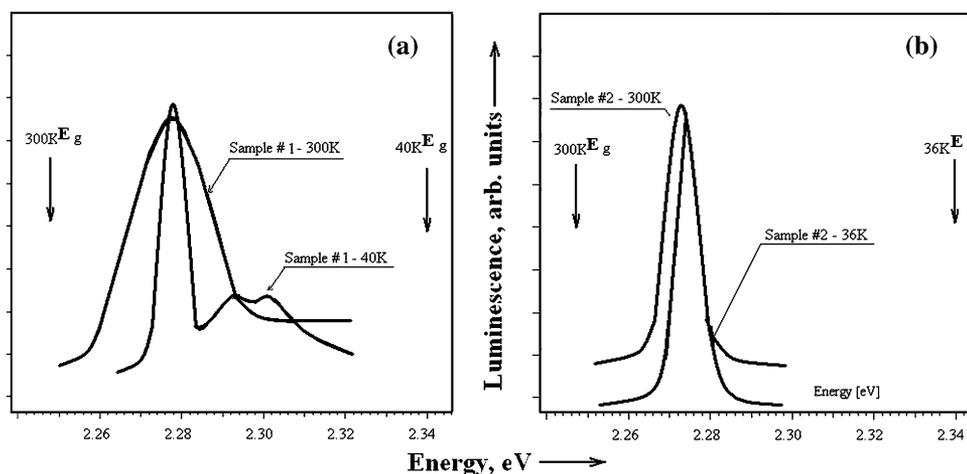


Fig. 5. Luminescence of the long-term ordered GaP:N crystals. N concentration is of the order of  $10^{18} \text{ cm}^{-3}$  for sample 1 (a) and three times more for sample 2 (b).

GaP:N:Sm system and bright luminescence at room temperature.

Figure 5a and b shows that GaP samples 1 and 2 with different concentration of N demonstrate the same, independent of temperature, spectral position of the luminescence band above (300 K) or below (36 K to 40 K) the forbidden gap. At low temperatures, N traps, located just below the bottom of the conductivity band, effectively capture nonequilibrium electron-hole pairs and due to this fact the luminescence is absent above the forbidden gap. At room temperature, these shallow traps are inefficient; therefore, direct recombination of nonequilibrium electron-hole pairs accompanied by optical phonon absorption as well as an equitable decrease of the forbidden gap leads to luminescence with a maximum located nearly at the same position as at low temperatures.

During these 40 years the impurities in our doped GaP crystals have created a superlattice with a period that depends on their concentration.

The observed increase and narrowing of LO modes while the TO modes remain unchanged indicate that the high concentration of various impurities in the GaP crystals aged for 40 years did not distort the crystal lattice. The fact that no bound exciton pairs were observed and that the position of the narrow zero-phonon line A was shifting along the luminescence spectrum as a function of the nitrogen concentration (see Fig. 2a) clearly support the statement that the impurity atoms are distributed equidistantly due to an anticlustering process that took place over the 40-year time period. As a result, the nitrogen atoms formed a cubic crystal superlattice because they substitute host phosphorus atoms in a perfect, diamond-like cubic lattice of GaP. It appears that the nitrogen impurity atoms also help to improve the host GaP lattice, as concluded from the extremely narrow phonon peak. In disordered crystals, impurities play a destructive role, specifically at high concentrations. By periodically substituting host atoms or occupying interstitials of the

host lattice, the impurities improve the quality of the host lattice and participate substantially in defining its phonon spectrum. Even though we have not performed calculations of the strength and harmonicity of the phonon modes in the impurity modified lattices, the experimental data testify that host atoms in the aged crystals are in near-perfect order. Obviously, the periodically disposed impurities fortify the host lattice, making the vibrations of short chains more harmonic.

Of course, the relevant anomalous soft X-ray diffraction at the nitrogen K-edge could provide a direct confirmation of the creation of an impurity superlattice. We plan to perform some of these experiments at the ELETTRA synchrotron, Trieste, Italy.<sup>32</sup> However, the detection of the impurity diffraction at the low impurity concentration compared with the four orders of magnitude greater concentration of the host atoms seems to be rather problematic. Therefore, we suppose that indirect but more sensitive luminescent and RLS methods will provide an efficient and exhaustive approach.

### CONCLUSIONS

The investigation and application of the long-term ordering (LTO) in the GaP:N system are of great interest because, besides their fundamental scientific interest, these phenomenon provide a unique opportunity to improve the quality of artificially grown crystals and to discover new, useful properties that are applicable for semiconductor device manufacturing.

The results of the investigation of these phenomena obtained with this unique collection of ordered GaP single crystals give a new approach to the fabrication of devices for applications in optoelectronics and microelectronics. The choice of aged crystals is explained by the fact that they have very stable characteristics in time (which yields low degradation of devices) in comparison with new samples. Some of them (GaP:N and GaP:Bi) at the relevant excitation will contain significant light capacity and develop low-threshold nonlinear effects in a dense ordered bound excitonic phase. In particular, the ordered high-density bound exciton system with approximately the Bohr radius distance between the excitons represents a crystalline excitonic phase that has unique and highly useful properties. Devices fabricated from the aged crystals will be considerably more tolerant to degradation than those fabricated from fresh analogues. It was also shown by us<sup>24,25</sup> that long-term ordering in some cases can be replaced by a short-time temperature treatment of fresh crystals.

The main conclusion, confirmed after 40 years of study, is that the impurities in doped GaP create a sublattice with a period that depends on their concentration. During diffusion, N impurities substitute for P atoms in the host lattice of GaP and overcome energy barriers of the order of 1 eV under

normal pressure and temperature. Evaluations show that 10–15 year intervals are necessary to monitor the remarkable changes in the quality of the crystals.

With the significant recent progress in semiconductor thin-film deposition and growth techniques, there is obviously no longer a need to wait for such ordering to occur. Now it is possible to generate a crystal-like excitonic phase in the artificially ordered GaP:N system. For instance, a superlattice from GaP/GaP:N with a period on the order of the Bohr radius, which is equal to 5 nm, can be prepared by molecular-beam epitaxy (MBE) in combination with laser-assisted epitaxy (LAE).<sup>19,21,33,34</sup>

In any case, independently of the method of creation, the impurity-modified crystal lattices and the excitonic (as well as biexcitonic) phase with translational symmetry are very interesting objects, the properties and possible applications of which are now under investigation. It was the intention of this work to show the effects of impurity ordering on the phonon spectra and luminescence of these materials.

Thus, the principal result of this protracted study is the discovery of two unknown earlier crystal states:

- (1) a modified crystal lattice in which the impurities have become an intrinsic component and periodically substitute the host atoms or occupy interstitials: a new type of high-quality crystal lattice;
- (2) a crystalline excitonic phase on the basis of an impurity superlattice with a period equal to the Bohr dimension of the exciton: a new nonlinear optical medium for the accumulation, conversion, and transport of light energy.

Our work has been being carried out for years; however, the most important results for device applications will be obtained only now with the recent progress in the preparation of film and multilayered structures. We hope they will have significant commercial value as it provides an absolutely new optical medium and product.

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