OPTICAL CHARACTERIZATION OF LONG -TERM ORDERED AND NANOCRYSTALLINE GaP

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Abstract

The paper generalizes some results of the United States/Moldova program on advanced composite organic and semiconductor light emitters. High density exciton system bound to N impurity superlattice grown by modern technologies and GaP:N, GaP:N:Sm nanocrystals distributed in transparent fluorine-containing polymers will be used as the base elements for new generation of optoelectronic devices. The work seeks to expand further the applications of GaP itself through the formation of nanocomposites.

Classic and new methods are applied for preparation of GaP:N nanoparticles with the controlled dimensions developed clear quantum confinement effect. The long-term ordered bulk GaP crystals as well as their nanoparticles have been investigated by TEM, XRD, Raman scattering, and luminescent methods.

The evolution of the Raman Light Scattering and luminescence spectra is reported from pure and doped GaP single crystals grown over 40 years ago and evaluated approximately every 15 years. For the first time bright luminescence of the nanoparticles and "hot" luminescence of the ordered crystals due to their high perfection and low level of nonradiative recombination are detected at room temperature in the wide spectral region at the photon energies considerably more than the indirect forbidden gap compared with bulk just prepared crystals where the luminescence is absent at room temperature and limited by the edge of the indirect forbidden band at low temperatures. Independently on temperature the unique ordered GaP:N:Sm system generates with high efficiency luminescence of the N recombination centers uniformly intermixed with Sm activators.

Our results clearly indicate the long-term impurity ordering and formation of a new type of crystal lattice where periodically disposed impurities located instead of host P atoms or in interstitials modify, improve and essentially change luminescent characteristics.

To the best of our knowledge, this is the longest running set of experiments on a single set of samples to study the temporal effects of crystal lattice and impurity ordering.

1. Introduction

After approximately 15 years since these samples were last monitored (Unversita degli studi, Cagliari, Italy [1]) and more than 40 years since they were prepared (State Technical University, St. Petersburg, Russia [2]) this work undertakes the next cycle of investigation of

the long-time ordering of impurities in the GaP crystal lattice. Here we compare the luminescence and the Raman light scattering from GaP crystals measured recently and the years ago in order to investigate the evolution of the crystal lattice and the character of impurity distribution. Now and then we used the same GaP crystals grown by one of the authors (S. L. P) in 1963-1966, for the first time described in 1966 and 1968 [2, 3] and then presented at the relevant conferences around the world [4-10 and others]. This paper based on the plenary talk of the same name at the 3rd International Conference on Materials Science and Condensed Matter Physics (October 3-6, 2006, Chisinau, Moldova) presents a part of the US/Moldova Program on advanced light-emissive sources on the base of transparent robust fluoropolymer and GaP nanoparticles [7-10].

2. Review of experimental results and discussion

2.1. Organic polymers and importance of PFCB polymers in integrated optics

Organic polymers are increasingly attractive alternatives to inorganic materials in many photonic devices such as, for example; switchers, optical interconnects, splitters, and surface relief structures. Polymers offer low cost fabrication, adequate transparency in the visible and near-infrared spectra, and versatility in structures and grades to cover a broad range of property values providing extensive device design flexibility.

Electro-optic polymers have been the focus of intense research for well over a decade. EO polymer modulators, in fact, could meet current and future requirements for high data rate links between satellites, aircraft, and ground-based platforms. The aim of this polymer collaboration is to advance synthetically versatile and scalable high temperature optical fluoropolymer technology to yield light emitting components.

Development of a unique fluoropolymer technology based on perfluorocyclobutyl (PFCB) aromatic ether repeating units, for which thermomechanical robustness and solution processability are not compromised, has been undertaken [11, 12]. Perfluorocyclobutyl (PFCB) polymers and copolymers have demonstrated in the laboratory a superior combination of optical and structural properties including: low transmission loss at 1500 nm, unprecedented melt and solution or solventless processability, and tailorable refractive index and thermooptic coefficients. Initially developed at The Dow Chemical Company [13], the general classes of PFCB polymers were originally targeted for microelectronics applications.

Optical absorption of investigated homopolymers was studied in the UV-infrared ranging from ~ 200 nm to 3200 nm [14]. Of particular note is the lack of absorption peaks in the wavelength range of interest for telecommunication applications. PFCB polymers, in general, show great potential for low loss photonic applications. The refractive index is completely stable after multiple heat/cure cycles and continued heating at 200 °C.

Figure 1 exhibits drawn fluoropolymer fiber (top left), its illuminated cross-section (bottom left) as well as surface SEM images of micro-transfer molded and classically defined PFCB structures via soft (top right) and plasma etch (bottom right) lithography techniques. Due to the excellent processability of PFCB polymers, recently microtransfer molding of waveguide structures has been pursued [5, 6]. Specifically, PFCB polymers have been used to fabricate optically diffractive line-gratings with 0.5 μm feature sizes by direct micromolding using only a photolithographically generated silicon master. This “negative mold-free” technique permits feature reproduction at submicron size scales (Figure 1, top left), proves to be practical means for rapidly generating planar photonic structures for visible and near IR bands.

The Center for Optical Materials Science & Engineering Technologies (COMSET) at Clemson University also elaborates the micromold core/clad waveguide structures [15, 16]. This technique demonstrates that sharp edges between core and clad interfaces can be achieved. As clearly shown, the interface between core and clad represents a maximum intimacy as expected due to the very similar copolymer composition for core and clad. This feature of PFCB copolymers demonstrates a unique and exciting opportunity for optical device micro-integration. Also the PFCB core/clad waveguide structures have been generated by classical Reactive Ion Etch (RIE) techniques (oxygen plasma). Clearly resolved core structures have been generated and the successful over cladding with excellent gap fill resulting in the first all PFCB waveguide has been demonstrated.

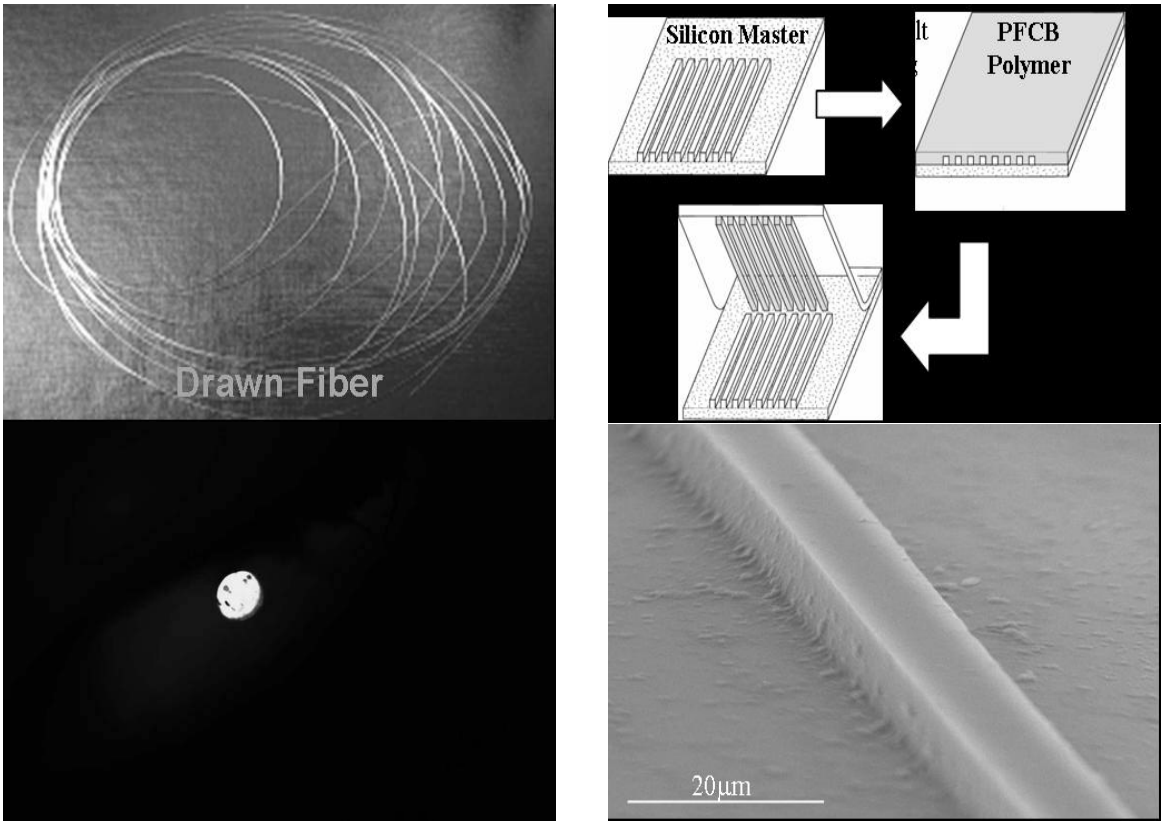

Figure 1. Some PFCB fluoropolymer device structures: fiber (top left), its illuminated cross-section (bottom left), surface SEM images of micro-transfer molded and classically defined PFCB structures via soft (top right) and plasma etch (bottom right) lithography techniques.

These initial results demonstrate waveguides without active functionality in order to establish inherent loss characteristics (underway) and thermo-optic device design criteria. Once demonstrated, the microfabrication methods will be applied to the novel PFCB-EO.

2.2. Characterization of GaP nanoparticles obtained by aqueous synthesis [10]

Figure 2 shows the TEM image of GaP nanoparticles obtained by the aqueous synthesis. One can see clusters with the dimensions of the order of 100 nm composed of GaP nanoparticles, having characteristic dimensions less than 10 nm. In Figure 3 one can see a considerable evolution of Raman spectrum of the nanoparticles compared with the bulk crystals. Instead of

transversal TO and longitudinal LO lattice phonons of bulk GaP at 365 and 402 cm^{-1} respectively (see curve 1 in Figure 3) the nanocrystals demonstrate their own weak and considerably shifted phonons. Note that opposite to the initial product of the aqueous synthesis (curve 2), only thoroughly annealed initial mixture demonstrates clear Raman spectrum (curve 3). Figure 4 demonstrates a considerable shift of the luminescence of nanoparticles to high energies of photons compared with the luminescence of pure bulk GaP crystals - the nano crystals have the maximum of luminescence at 2.35 eV instead of 2.1-2.2 eV characterizing the bulk material.

Thus, we demonstrate here that the nanoparticles obtained by a simple aqueous synthesis have the controlled dimensions at which the quantum confinement is clearly observed. In particular, their luminescence is detected at room temperature in the wide spectral region 2.0-2.5 eV compared with freshly prepared bulk material [3] where the luminescence is limited on the side of the high energies of photons by the edge of the indirect band gap of GaP.

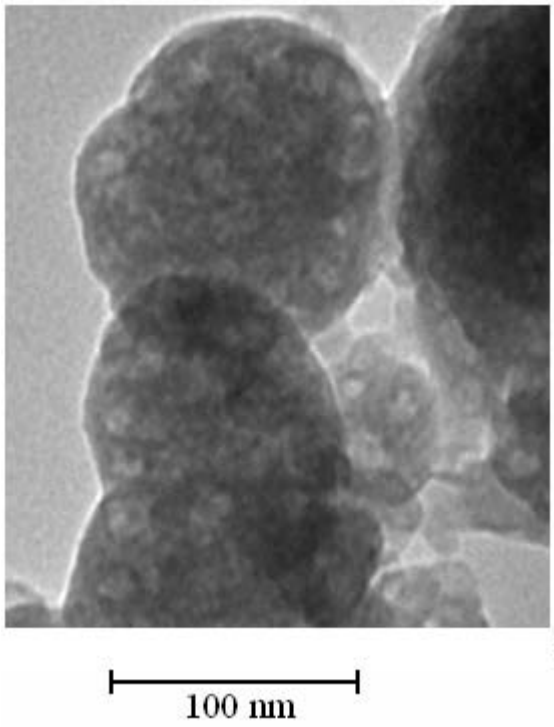

Figure 2. TEM image of clusters from GaP nanoparticles, obtained by aqueous synthesis.

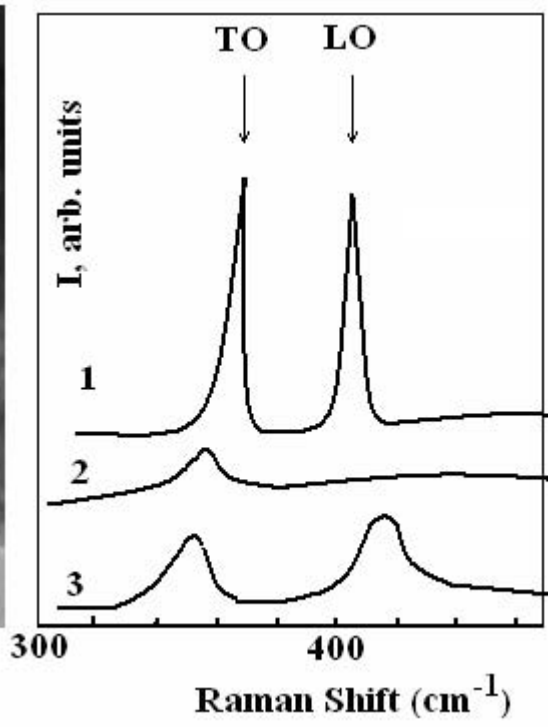

Figure 3. Raman spectra of GaP nanoparticles before (2) and after (3) annealing at Ar flow compared with bulk crystal (1). TO, LO – transversal and longitudinal optical lattice phonons. 300K.

2.3. Long-term ordering in GaP crystals

Continuing the monitoring of properties of our GaP single crystals grown 40 years ago [2], in 2005 - 2006 we have been studied their luminescent properties in comparison with the data obtained in the sixties, seventies, eighties, and nineties of the past century [1-6] as well as with the luminescence of the described above nanocrystals [10]. Here we discuss only some principal results - the details of this monitoring will be presented later in [17] and elsewhere.

Note that due to a lot of defects and a highly intensive non-radiative recombination of non-equilibrium current carriers, initially and for a long time [1, 3] the luminescence of fresh doped and undoped crystals could be observed only at the temperatures 80K and below. Then

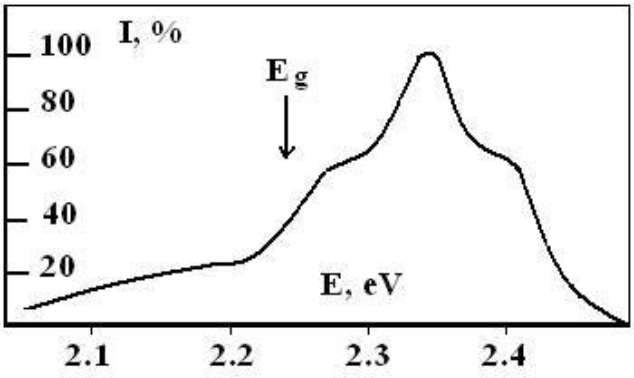

Figure 4. Luminescence of GaP nanoparticles with the dimensions of the order of 10 nm. Luminescence is observed at room temperature; compared with bulk crystals its maximum is shifted to high energies of photons (E_g is the position of the forbidden gap at 300K).

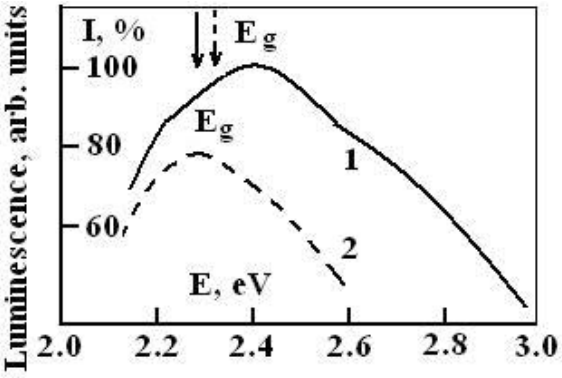

Figure 5: Luminescence of perfect bulk GaP single crystals prepared in 1966 and measured in 2006. Luminescence is observed at room temperature and its maximum is shifted to high energies of photons. The position of the forbidden gap E_g at 300K and 80K is marked by arrows, dotted arrow – 80K.

the luminescence band and lines were seen always at the photon energies less than the value of the forbidden gap. Now luminescence of the long-term ordered bulk perfect crystals alike with the mentioned above nanocrystals is clearly detected in the region from 2.0 eV and until 3.0 eV at room temperature (see Figures 4 and 5, curve 1). The shape of the luminescence band and its maximum highly depend on the intensity of excitation. As before the luminescence at 80K (Fig. 5, curve 2) has the excitonic band maximum below the position of the forbidden band edge, but now a part of the luminescence can be seen above the edge.

We suppose that in the perfect bulk crystals at 300K this considerable extension of the region of luminescence to the high energy side of the spectrum is connected with a few reasons. Among them note very small concentration of defects and the relevant low contribution of the non-irradiative electron-hole recombination, considerable improvement of crystal lattice, high transparency of perfect crystals, low probability of phonon emission at rather high temperature and participation of direct band-to-band electron transitions.

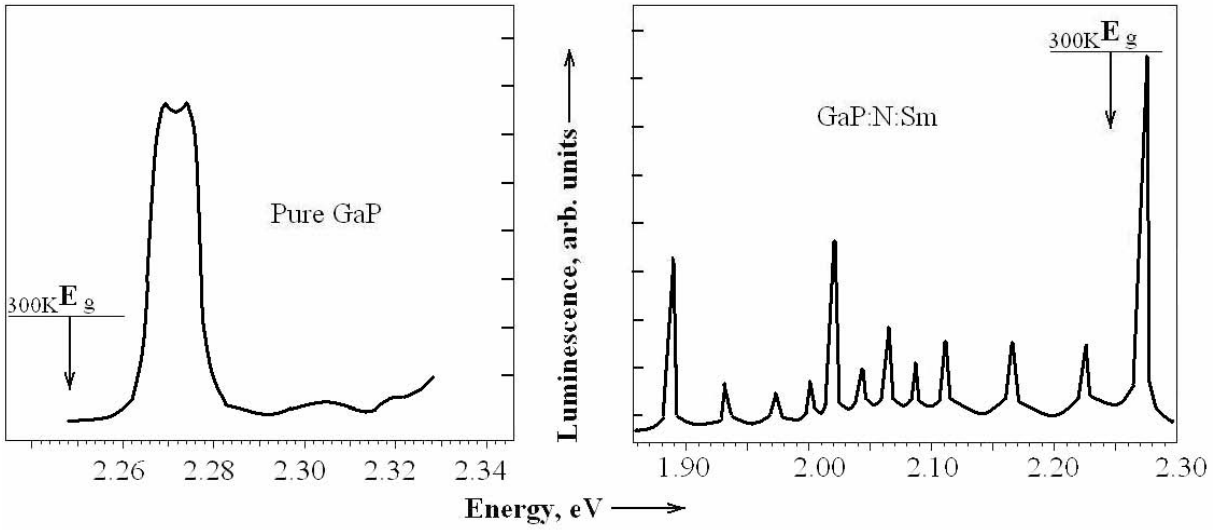

Figure 6. Luminescence of the ordered pure GaP (left) and GaP:N:Sm (right) crystals at room temperature.

Figure 6 (left) demonstrates “hot” luminescence through indirect forbidden gap from pure long-term ordered perfect GaP single crystal. The momentum conservation rule is fulfilled due to participation of the lattice optical phonons. On the right one can see Sm emission lines in presence of uniformly intermixed N recombination and Sm activator centers. For the first time these GaP:N:Sm crystals have been investigated in [18] when their luminescence could be observed only at 80K and below. Note that the ordering gives a uniform mixture of Sm and N impurities that according to [19] provides up to 100% quantum efficiency of radiation from GaP:N:Sm system and bright luminescence at room temperature.

Figure 7 shows that GaP samples 1 and 2 with different concentration of N demonstrate the same temperature-independent spectral position of the luminescence band above (300K) and below (36-40K) the forbidden gap. At low temperatures N traps, located just below the bottom of the conductivity band, effectively capture non-equilibrium electron-hole pairs and due to this fact the “hot” luminescence is absent. At room temperature these shallow traps are inefficient; therefore, direct recombination of non-equilibrium electron-hole pairs accompanied by optical phonons absorption as well as an equitable with the phonon energy temperature decrease of the forbidden gap leads to the luminescence above the forbidden gap, but with the maximum located nearly at the same position as at low temperatures.

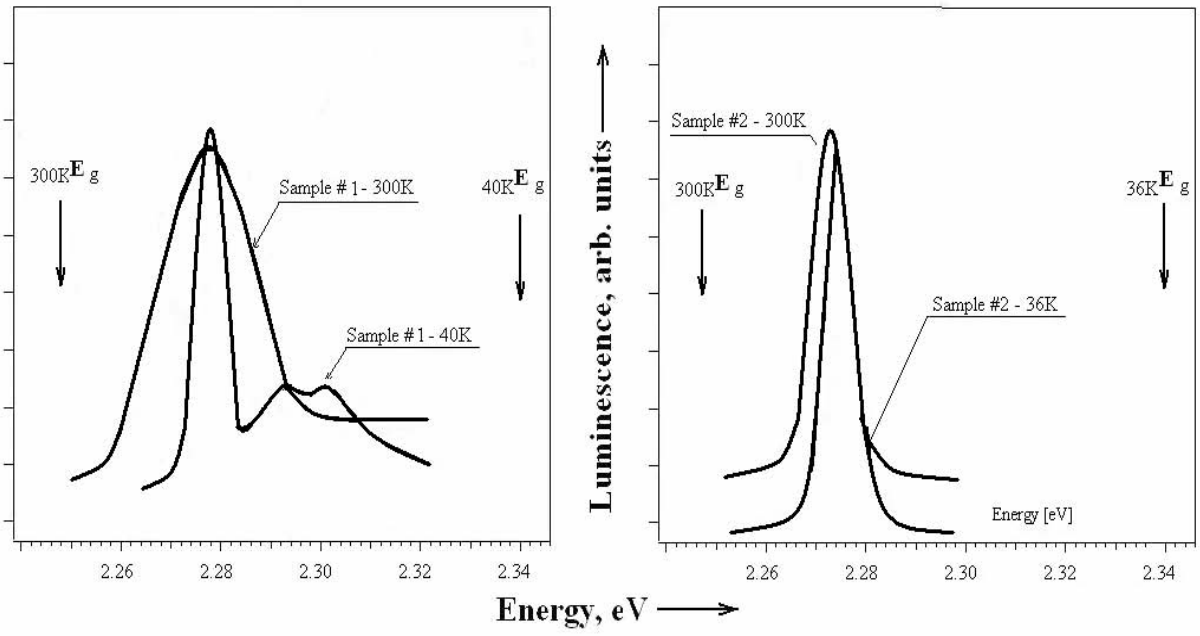

Figure 7. Luminescence of the long-term ordered GaP:N crystals. N concentration is of the order of 10^{18} cm^{-3} for sample #1 and 3 times more for #2.

The first discussion of the temporal and concentration evolution of the initial distribution of nitrogen atoms in a GaP lattice was made using fluorescence measurements [1, 5]. The distribution of N impurities with equal impurity spacings, r_{NN}, leads to a systematic shift of the zero-phonon line (also called the A line) of a single exciton bound to the N atom in GaP and its lattice phonon replica with N impurity concentration [20]:

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

where E_N is the energy of the A-line position at $r_{NN} \to \infty$ and E_{NN} is its energy at some non-zero nitrogen concentration. The proportionality constant β serves to make the equation dimensionally correct and equals 13 if E_N, E_{NN} are given in units of eV and r_{NN} in units of Å.

Figure 8(a) (spectra 1–3) shows a shift of the zero-phonon line depending on N concentration measured in the crystals 20–25 years after their preparation (1989–1993). This results show that to this time the N impurities are located on equal r_{NN} spacings. In contrast to the ordered case, newly grown GaP:N crystals exhibit broad distributions in r_{NN} values, the most obvious result being a concentration broadening of the zero-phonon line and its phonon replica (Figure 8(a), spectrum 4).

Other evidence for the ordered character of the distribution of the impurities is the lineshape of the zero-phonon line and its phonon replica: they are broad in newly prepared samples and narrower in long-term ordered crystals (see Figure 8(b)). Further, 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 impurity concentration 10^{18} cm^{-3} are equivalent and equal to app.10 nm, while for these NN-pairs the spacings range from 0.345 nm (NN_1) to 1.219 nm (NN_{10}) [21].

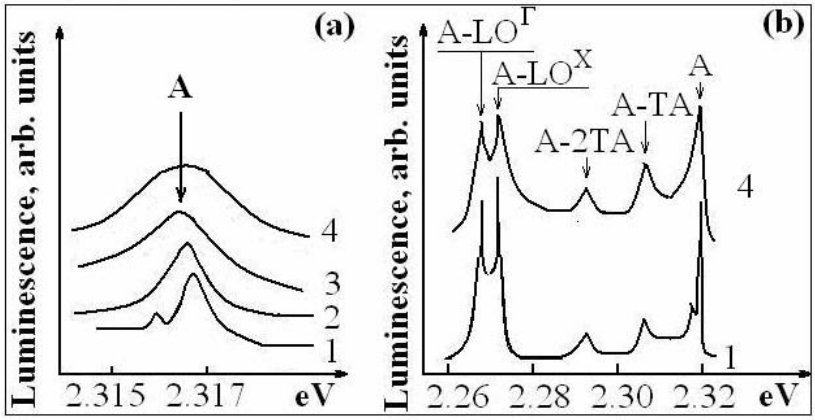

Figure 8. Evolution of the zero-phonon line of bound exciton A as a function of N concentration. (a) 15K. 1-3: ordered crystals. 4: unordered. 1-4: N_o = 10^{17}; 10^{18}; 10^{19} and 10^{18} cm^{-3} concentration of N, respectively. (b) 15K. Zero-phonon line and its transversal acoustic (TA) and longitudinal optic (LO) phonon replica.

Now let us consider the present state of the crystal lattice in comparison with the data obtained in 1989–1993 [1, 6]. Figure 9 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 the 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 (only a very small shift ~0.3 cm^{-1}, which is not resolved in the scale of Figure 9). 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.

Concerning the general differences in the spectra produced by the ordered and disordered forms of the crystals, note in accordance with [22] that the spectrum of the most ordered heavily N-doped crystal (spectrum 2 in Figure 9(b)) shows a considerably more intense narrow LO line than the less ordered pure or doped crystals (spectra 3 and 4 in Figure 9(b)). Whereas the distribution and the environment of the P or N anions at a particular site in the unit cell in the ordered crystal are uniform, the great variability 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, are the peaks denoted by us here as LA, 2TO and TO + LO (Figure 9(c)). 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 [23], and two pho-

non processes of 2TO and TO + LO emission can also be observed in perfect crystals [24]. 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.

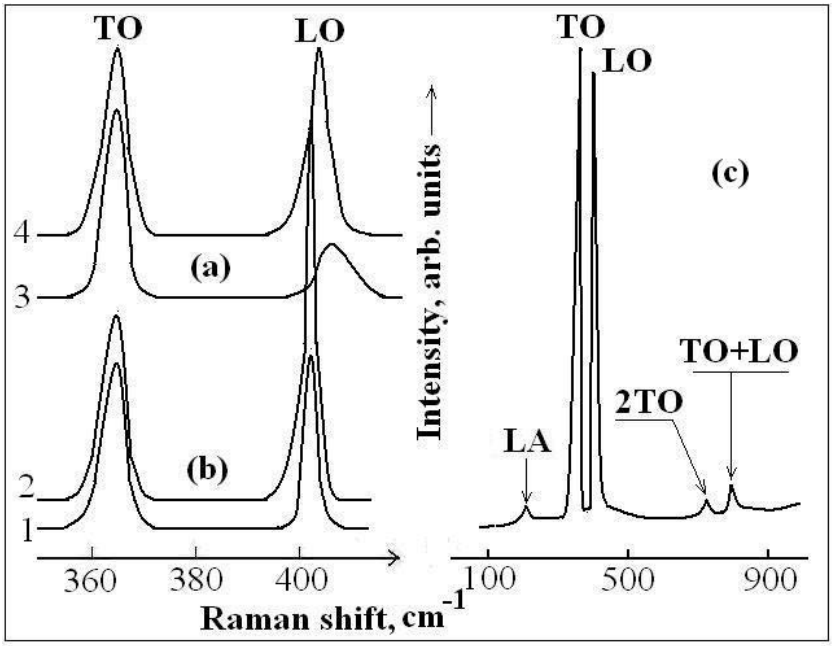

Figure 9. Raman spectra in GaP and GaP:N in 1989-1993 (a) and in 2006 (b, c). 1, 4 – pure GaP, 2, 3 – GaP heavy doped with N. Spectra 3, 4 are taken from [6] and obtained by one of the authors (SLP) in 1991.

Figure 10 provides the Raman spectra obtained recently (2005–2006) from pure and heavily doped GaP at 300 K (a) and 80 K (b). It can be seen only in the GaP:Bi crystal at 300 K that a very narrow LO phonon is slightly shifted (approximately 2 cm^{-1}), while the TO and LO peaks maintain their spectral positions at 80 K for the pure and doped GaP crystals independently of the type of impurity and its concentration. 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. Note that these results are obtained despite the fact that the maximum concentrations of N, Sm, and Bi in these crystals are close to their limit of solubility (~10^{19} cm^{-3}), the masses of impurity atom are very different (the atomic weights for N, Sm and Bi are 14, 150, and 208, respectively) and the N and Bi impurities substitute P sites in the crystal lattice whereas Sm occupies interstitials.

The position and the line-width of the TO line in the ordered crystals do not depend on type and concentration of impurity or on temperature. The observed phonon lines are slightly broader than those given in [23] because an excitation at 514 nm was used here instead of at 632.8 nm [23] where the excitation volumes are different. In the experiments reported here and in [23] the crystals had the same (111) orientation, but the authors of [23] worked with newly grown crystals containing impurity concentrations of approximately 10^{17} cm^{-3}, whereas here aged crystals were used with a wide set of impurity concentrations ranging from 10^{16} cm^{-3} to more than 10^{19} cm^{-3}. The temperature-independent TO line-width in the aged crystals implies that the impurities do not perturb the order of the lattice, which is possible only for a very uniform environment.

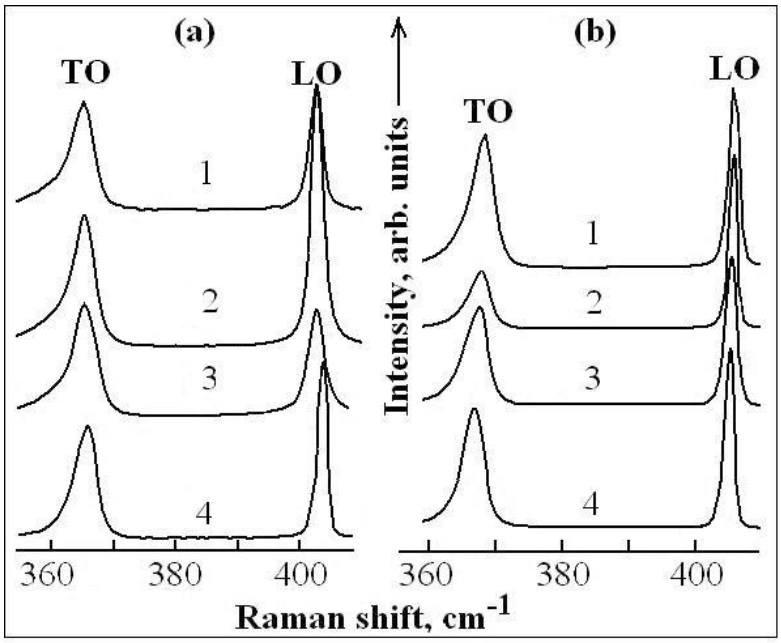

Figure 10. Spectra of Raman light scattering from pure and doped GaP at 300K (a) and 80K (b). 1: Pure. 2-4: GaP doped with N, Sm, and Bi, respectively.

It is known that the broadening and frequency shift of the phonon lines are due to anharmonicity of the lattice vibrations and disorder in the crystal. Comparison between the experimental data and theories of the broadening and shift of the phonon lines during heating of the crystal showed that the experimental dependences can be explained by the contributions from lattice anharmonicity of third and fourth orders and a broadening of the TO phonon lines due to the disordered nature of the crystal [23, 25]. According to [25, 26] one can also assume that small disorder in crystals leads to a shift and broadening that are independent of temperature and the line-shape is close to Lorentzian, but the effects due to anharmonicity depend strongly on temperature. Note that the measured TO line-shapes in the current crystals are closer to the Lorentzian shape than in [23] and the LO lines are narrower in the crystals with larger impurity concentrations. This implies that the anharmonicity of the lattice vibrations in the presence of ordered impurities is less than that in crystals with disordered impurities. An increase in temperature only slightly distorts the TO line-shape in these crystals, also implying that the anharmonicity is weak. Considering these results, it is concluded that the anharmonicity is larger in perfect crystals than in doped crystal with periodically disposed impurities.

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

3. Conclusion

To the moment we have accomplished the 40 years cycle of investigation on the impurity ordering and improvement of quality of the host lattice.

The main conclusion, confirmed after 40 years of study, is the statement that the impurities in doped GaP create a sub-lattice with a period that depends on their concentration. The motive forces of these changes are gradient of impurity concentration and mechanical strength

leading to the diffusion of impurities, their uniform distribution and creation of impurity superlattce. During the diffusion N impurities substitute P atoms in 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 for monitoring of the crystals to clearly observe the long-term ordering process.

By periodic substituting for host atoms (N, Bi) or occupying interstitial sites (Sm) in the host lattice, the impurities become an intrinsic component of a modified crystal lattice; they participate in the formation of a "new" phonon spectrum, improve and considerably change luminescence. 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. The periodically disposed impurities fortify the host lattice making the vibrations of short chains more harmonic. It appears that the nitrogen and other impurity atoms help to improve the host GaP lattice, as concluded from the extremely narrow phonon peak.

In disordered crystals, impurities play a deleterious role, specifically at high concentrations. In the long-term ordered crystals the observed increase and narrowing of LO modes while the TO modes remain unchanged indicate that the high concentration of various impurities in GaP crystals aged for 40 years does not distort the crystal lattice.

The facts that no pair bound excitons were observed and that the narrow phonon line A was shifting along the luminescence spectrum, depending upon nitrogen concentration (see Figure 8(a)), clearly support the statement that the impurity atoms are distributed equidistantly due to the anti-clustering 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 that are in a perfect, diamond-like cubic lattice of GaP.

The ordered crystals with the host lattice modified by impurities could be very useful in various optoelectronic applications. Noted here are only a few potential applications in light emissive device structures. The properties of these structures will be stable and independent of time. Uniform distribution of the recombination (N) and activator centers at the optimum concentration will yield the maximum efficiency for light emission. Further investigations of the quasicrystalline state of excitons (or bi-excitons) bound to an impurity superlattice with a period equal to the Bohr radius will be very interesting and useful because they should greatly strengthen the non-linear optical effects at low excitation intensities. The ordered excitonic phase, having a very small threshold for different non-linearities, gives new fantastic opportunities for accumulation, conversion, and transport of light energy [6, 27].

With the significant recent progress in semiconductor thin film deposition and growth techniques there is obviously no longer a need to wait for such an ordering to occur. Now it is possible to generate crystal-like excitonic phase in artificially ordered GaP:N system, and it gives the unique opportunities not waiting of natural ordering for decades of years to elaborate new generation of photonic devices for transportation, storage, and transformation of high density light energy. For instance, a superlattice from GaP/GaP:N with a period of the order of the Bohr radius, which is equal to 5 nm, can be prepared by molecular beam epitaxy (MBE) or by MBE in combination with laser assisted epitaxy (LAE). Combined methods of laser assisted and molecular beam epitaxies Elaborated by us [28-31] will be applied to fabrication of device structures with artificially ordered impurities; equally with classic methods they will be used for preparation of new types of nanoparticles and their composites with the fluoropolymers.

Further, the preparation of a two-dimensional arrangement of N impurities in a GaP film is difficult but also possible with the help of ion lithography. Certainly, nowadays this tech-

nique is at the frontier technological possibilities, but within the next 2–3 years some very important results are likely to be obtained in this field.

In any case, independently on the method of creation, the impurity-modified crystal lattices and the excitonic (as well as bi-excitonic) 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 of these materials.

Thus, we pretend to discovery of two crystal states unknown earlier:

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

Our work has been carried out for years, however, the most important results for device application will be obtained only now with the recent progress in preparation of film and multi-layered structures.

We hope this project will have significant commercial value because it gives an absolutely new optical medium and product.

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