Synthesis of Recording Medium for Multilayer Photoluminescent Disc

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***Abstract*-A method which allows separating of parasitic signal at readout system of photoluminescent multilayer disc was proposed. Photoluminescent recording medium based on nanostructured pyrazoline dyes was synthesized. Advanced capabilities for engineering of synthesized luminophors optical properties through laser annealing and doping were analyzed. Stability of synthesized luminophors photoluminescent spectrums was shown.**

Keyword- Multilayer Photoluminescent Disc; Recording Medium; Pyrazoline Dye; White Zeolite; Quantum Yield

I. INTRODUCTION

Optical disc is the most prominent media for long-term storage of nonvolatile digital information. Unlike flash-memory and magnetic recording, it codes data by microrelief structure (read-only memory) or local thermal damage of the reflective layer (recordable format). It is much more reliable than the use of ferromagnetic remanent magnetization effect or record information by varying of electric charge at floating-gate transistors array. Nowadays the methods for optical recording are further improved by the development of high-stability materials for substrates and high-precision lens actuators; it also should be noted that optical disc can be restored by means of microscope.

The rapid development of flash-memory and magnetic recording technologies, however, caused necessity to bring new format of optical discs into accordance with the requirements of superdense recording. So far, the improvement of optical media has been based on methods of area-density recording increase. It is well known that the resolution of laser recording and readout drives is determined by diffraction limit and diameter of focused beam (on $1/e^2$ level), and may be estimated by

$$d = k\frac{\lambda}{NA} \tag{1}$$

where λ is the wavelength of the probing beam, *NA* is the numerical aperture of the focusing lens and k is an aperture-dependent coefficient. Therefore, further increase of optical recording area-density is possible by means of short-wave lasers use (λ decrease), high numerical aperture lenses development (*NA* increase) and entrance aperture apodization (k decrease) which is though substantially limited and tends to cause probing beam intensity decrease. Trend analysis of optical discs development shows that methods of area-density recording have got their limitations (Table 1).

TABLE 1 ANALYSIS OF OPTICAL DISCS AREA-DENSITY RECORDING INCREASE POSSIBILITIES

	CD	DVD	BD	Possibilities and problems of optical disc format improvement
λ, nm	780	650	405	Further shortening of laser wavelength requires UV laser use and tends to cause data reader size increase and possible destruction of plastic substrate of the disc.
NA	0.45	0.6	0.85	Further increasing of NA implies use of methods based on solid immersion lens and tends to cause significant increase of data reader's complexity and vulnerability.
Data density GB/inch	0.41	2.77	14.73	Significant area-density increase of optical discs is hardly feasible by usual means.

Significant increase of optical disc's information recording density could be obtained by volumetric recording methods. There are two types of volumetric optical recording with backward compatibility with optical discs of CD, DVD and BD format: multilevel and multilayer recording [1]. The multilevel optical recording implies recording more than one bit in each information unit, graduating readout signal and multiplying information capacity of a media. However, the multiplying of information capacity, at the same time, tends to decrease signal-noise ratio (SNR) and photodetector sensitivity threshold, because of the decrease of the minimal signal level. On the other hand, multilayer optical recording methods are partly used in reflective optical media (DVD and BD) could benefit from a new format of optically homogeneous discs that allows getting optical media data density comparable with one for flash-memory and magnetic recording.

II. THEORY

Photoluminescent multilayer disc (PMD) is a sandwich-structure of *N* information layers and *(N-1)* intermediate layers [2]. Unlike reflective dual-layer DVD- and BD-media, PMD is optically homogeneous and thus there is no re-reflected probing beam. To avoid parasitic signal being reflected by the surface of the disc information units (pits) for this type of media there

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was proposed to make from photoluminescent (PL) semitransparent material with a bigger value of stock shift. The parasitic signal of PMD-media is caused mostly by PL and absorption of pits from all of the layers except the readout layer where laser beam is unfocused. With the use of big amount of layers ($N \geq 10$), the SNR value will be unacceptably low. It has been suggested to distinguish readout signal using lock-in-like technique. The intermediate layer needs to be thick enough (50 μm or more) so that even the neighboring layer will be illuminated area that contains a big and stable quantity of pits n_p (Fig. 1). So, the neighboring layer parasitic signal amplitude I_p will also be stable and easy to be separated, and its intensity can be estimated with the concentration of pits at information layer k_p and the intensity of probing beam I_0. For standard compact disc pit's width, the signal amplitude can be calculated as:

$$I_p = k_p I_0 = \frac{w_p}{2w_t} I_0 \tag{2}$$

where w_p is the pit width and w_t is the track pitch width.

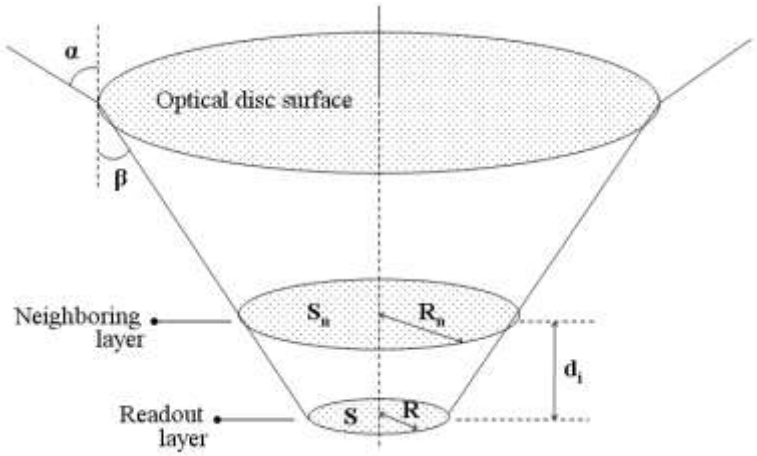

Fig. 1 Calculation of parasitic signal of PMD readout process

We proposed to deliberately maintain parasitic signal stable in order to separate systematic error. Parasitic signal amplitude variation ΔI_p is a random error of the readout process and can be estimated by taking in account the ratio of focused beam area S to the area of neighboring layer unfocused laser spot S_n:

$$\Delta I_p = I_0 \sum_{n=1}^{N} \frac{k_p S}{n_a S_n} \tag{3}$$

Thus, the thickness of the information layers depends on the pit's depth, while the thickness of the intermediate layers depends on FMD-drive objective lens aperture and must be big enough to distinguish the PL signals of different layers. It has been proposed to record information only by the lands (distances between the pits) length, while pits should be as small as possible to avoid undesirable absorption. Eqs. (2)-(3) shows the decreases of both I_p and ΔI_p values simultaneously. To uphold a stable parasitic signal during reading out from the edges of the PMD, it has also been proposed to build inner and outside peripheral areas which hold no data but simulate structure of the information layers. It was estimated that the total value of the inner and outside peripheral areas even for readout drive with a big NA is less then 1% of information layer area.

Another problem is the synthesis of appropriate PL recording medium. As well known, PL readout signal is spatially isotropic, so PMD readout drive gets just part of the probing beam energy:

$$I_{RO} = I_0 \eta k_A k_{RS} k_{LF} d\Omega / 4\pi \tag{4}$$

where dΩ is the PL radiation receipt angle, η is the PL quantum yield, k_A is the absorption factor, k_{RS} and k_{LE} are receiver systems and land exposure loss coefficients respectively. Thus, the problem of low signal rate becomes a major one, especially in the case of combining multilayer and multilevel recording methods and where one pit contains several bits of information. PMD-media is also characterized by its low readout rate caused by loss of time for PL relaxation. The only way to solve the mentioned problems is the synthesis of new dye with a high PL quantum yield and a low PL relaxation time.

III. EXPERIMENTAL RESULTS

To synthesize recording medium of PMD, pyrazoline "orange-red" UV dye 53 (Fig. 2) and base pyrazoline UV dye (Fig. 3) were used as base components. At the next stage, the pyrazoline dyes were dissolved in toluol and the obtained solution was implemented into polymethylmethacrylate or polystyrene matrix (Table 2). Most of the obtained luminophors were accepted as

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effective registration medium with high quantum yield of PL (60-70%), low PL relaxation time (100-140 ns) wide bandwidth of the PL and big enough absorption coefficient at short-wave lasers wavelength (Table 3). Experimental work was carried out on modified and automated grating monochromator assembled device LOMO "KSVU-12" and oscillograph C1-75 (time resolution t_r=7ns). The PL was excited by nitrogen laser ILGI-503 (wavelength λ=337 nm, pulse length t_p=10ns).

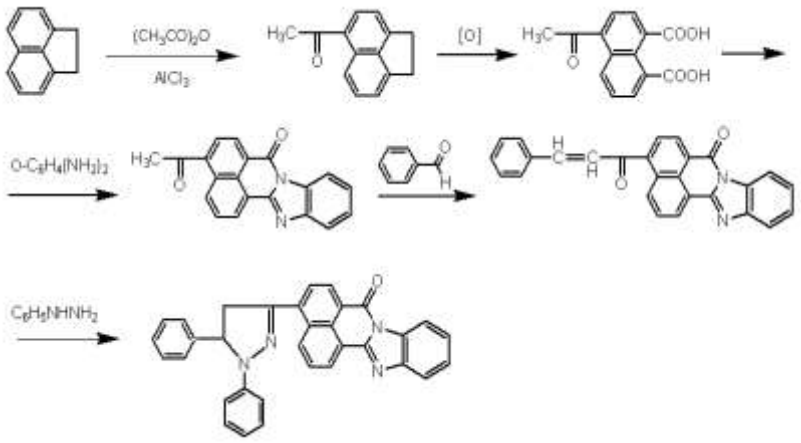

Fig. 2 Pyrazoline "orange-red" UV dye 53 (4–[1,5–diphenyl–2–pyrazolinil–3]–1,8– naphthoilen–1′,2′–benzimidazole)

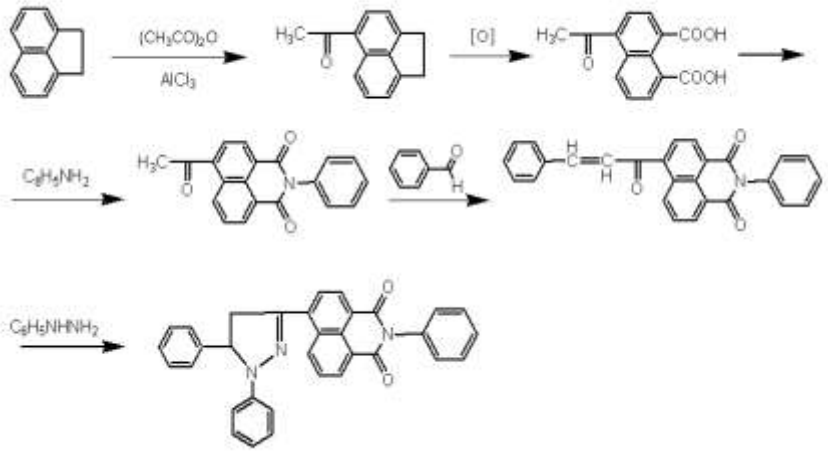

Fig. 3 Base pyrazoline UV dye 59 (4–[1,5– diphenyl–2– pyrazolinil –3]–N– phenyl phthalemide)

Experimental results also showed the existence of two-photon absorbance and PL effect. The criterion of two-photon PL effect consists in observing PL on frequency ω while excitation was on 2ω frequency. It can be obtained by using following equation:

$$\ln(I_{PL}) = a\ln(I_{pump}) + b \tag{5}$$

where $a \approx 2$ is the two-photon PL effect criteria coefficient (Table 3).

TABLE 2 CHEMICAL COMPOSITIONS OF PYRAZOLINE LUMINOPHORS

Pyrazoline dye	**Base component**	**Addition agent**
59M	pyrazoline "orange-red"	toluol
59HM	pyrazoline "orange-red"	toluol , 5% addition of polymethylmethacrylate
59HC	pyrazoline "orange-red"	toluol , 5% addition of polystyrene
53SM	base pyrazoline UV dye	toluol , 5% addition of polymethylmethacrylate
53SC	base pyrazoline UV dye	toluol , 5% addition of polystyrene

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TABLE 3 OPTICAL PROPERTIES OF PYRAZOLINE LUMINOPHORS

Pyrazoline dye	PL peak	PL relaxation time	Transmission at λ = 405 nm ("Blu-ray" readout length)	Two-photon PL effect criteria coefficient (a)
59M	580 nm	100 ns	21%	1.88
59HM	584 nm	80 ns	21%	2.13
59HC	549 nm	90 ns	22%	1.97
53SM	471 nm	50 ns	24%	1.92
53SC	508 nm	60 ns	23%	2.21

Further experimental research demonstrated advances of the significant characteristic improvement. The method was based on doping in pyrazoline dye 10% of white zeolite and thus inclusion organic dye molecules in the zeolite matrix. The zeolite nanopores have divided luminophor into nanoparticles (Fig. 4) and improved its optical characteristics, such as PL quantum yield and PL relaxation time (Table 4). Nanoscale images were obtained with atomic force microscope "Nanoscope IIIa Dimension 3000TM".

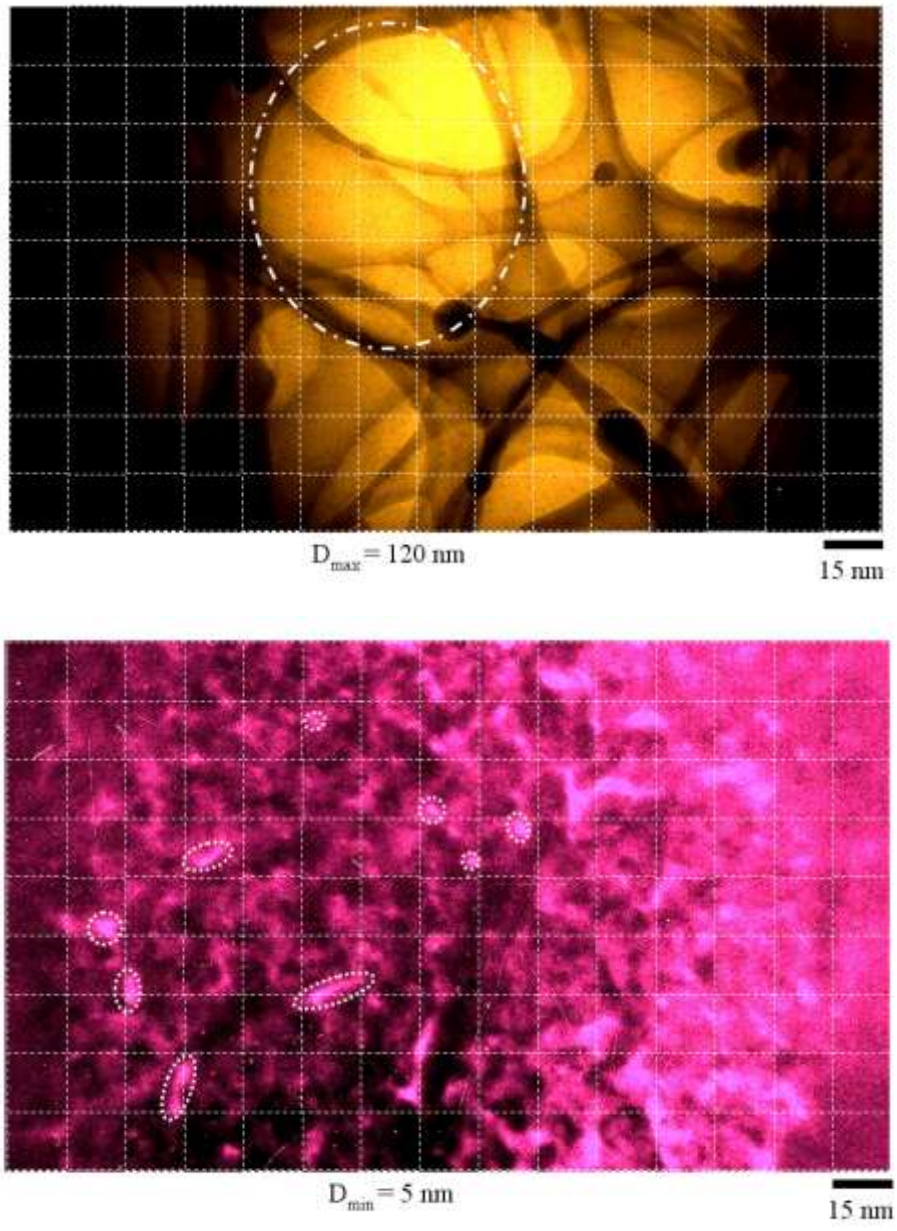

Fig. 4 Nanopatricles of pyrazoline dye 53SM with diameter D = 5-120 nm in matrix of white zeolite

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Growing of the PL quantum yield is caused by the quantum size effects, which change molecular energy structure of the dye [3-4]. It was shown that forbidden transitions were turning to partially allowed transitions. Organic dye absorption growth in this case is also concerned with the appearance of the new allowed transitions that made molecules relax to the lower energetic levels and absorb more of the incident light. As it was predicted such transitions also caused the rise of additional PL peaks, which were experimentally observed for 59M, 59HM and 53 SC pyrazoline dyes.

After focused laser illumination of obtained pyrazoline samples (wavelength λ = 940), irreversible PL spectrum transformation was revealed. Intensity of main and additional PL peaks (Table 4) was decreased, proving the possibility to use this type of medium for building recordable multilayer media (PMD-R).

The experimental results showed that kinetics of luminescence damped exponentially and were characterized by relaxation time of 50-100 ns (Table 3). Addition of the zeolite significantly decreased PL relaxation time (Table 4) but complex structure of the PL kinetics graph (Fig. 5) showed that pyrazoline has not completely filled in the zeolite pores. Additional laser annealing with power decreased to 10% to avoid luminophor bleaching allowed to further PL parameters of synthesized medium (Table 4).

TABLE 4 OPTICAL PROPERTIES OF NANOSTRUCTURED PYRAZOLINE LUMINOPHORS WITH LASER ANNEALING

Pyrazoline dye	Main peak intensity decrease after local bleaching with IR laser	Main peak intensity growth of nanostructured dye		PL relaxation time decrease of nanostructured dye		Transmission at λ = 405 nm ("Blu-ray" readout length)
		Before laser annealing	After laser annealing	Before laser annealing	After laser annealing	
59M	40%	25%	59%	11%	38%	11%
59HM	61%	17%	39%	20%	45%	9%
59HC	44%	26%	45%	33%	45%	9%
53SM	52%	37%	52%	36%	55%	7%
53SC	49%	41%	60%	20%	27%	8%

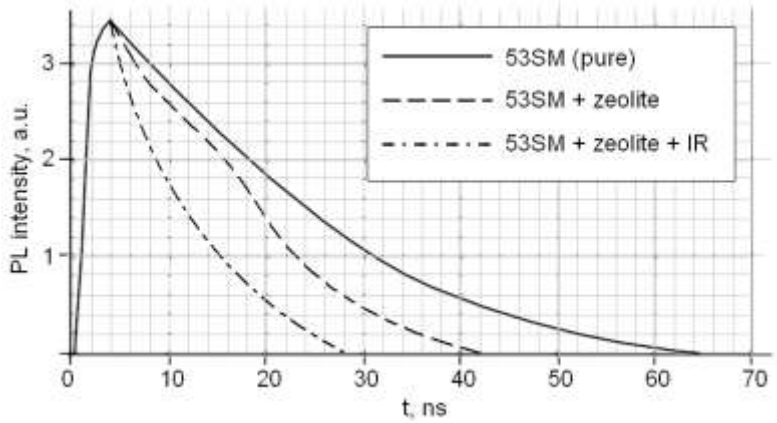

Fig. 5 Reducing of PL relaxation time for pyrazoline dye 53SM after inclusion into white zeolite matrix and laser IR anealing

Quantum-chemical calculation of pyrazoline dye electronic spectrums show that PL is specified by π-π*-electron transition with big oscillator strength (where π* is excited state of π-electron). It was experimentally confirmed by high PL quantum yield and low PL relaxation time of synthesized samples. Also, it is obvious that σ-electrons couldn't form PL spectrum of daylight luminophors while absorbance wavelength of π-transition should be at ultraviolet range. The wide peak of PL spectrum proves the emitting transition between lower levels of excited molecule to some vibrational levels continuum of unexcited molecule. Wavelength of the PL maximum is determined by the mechanism of interaction between luminophor molecules and matrix polymethylmethacrylate or polystyrene. It should be noticed that Stokes shift value and the appearance of secondary PL maximums are also caused by electron-phonon interaction of luminophor molecule at matrix, and it was shown that molecular bond between pyrazoline dye and polymethylmethacrylate is stronger than bond between pyrazoline dye and polystyrene. Focused laser illumination has probably caused thermal break-down of the molecular bonds and resulted in decreases of the main and additional PL peaks.

For the usage of synthesized luminophors as a recording medium of optical archive storage, it is necessary to check the stability of its optical characteristics. It is especially important for nanostructured medium because nanoparticles tend to migrate, and the migration leads to heterogeneity of the nanostructured material. Experimental results have shown that within the measurement accuracy range, the PL spectrum of pyrazoline dye did not change shape, bandwidth or amplitude for the last 10 years (Fig. 6). Synthesized samples were proved to be optically isotropic. The obtained stability was caused by fixing the dye nanoparticles at nanoporous matrix of white zeolite and the dye molecules at matrix of polymethylmethacrylate or

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polystyrene. For the same reason, local IR laser recording by luminophor bleaching (Fig. 7) and IR laser annealing (Fig. 8) also did not cause further material degradation.

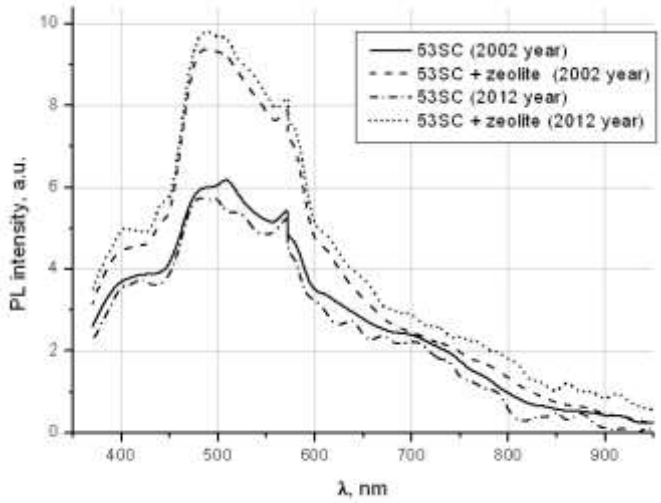

Fig. 6 Change of PL spectrum of pure and nanostructured zeolite doping pyrazoline dye 53SC during past time (10 years)

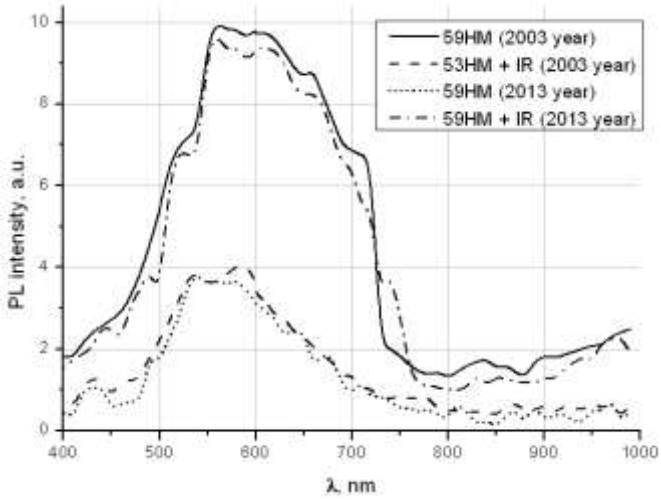

Fig. 7 Change of PL spectrum of pyrazoline dye 59HM and pyrazoline dye 59HM after IR laser recording during past time (10 years)

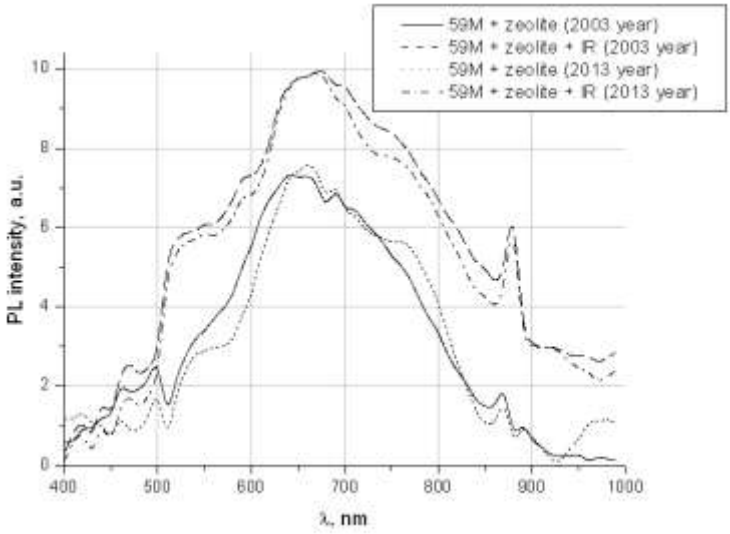

Fig. 8 Change of PL spectrum of nanostructured pyrazoline dye 59M before and after IR laser annealing during past time (10 years)

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It was also found that the two-photon absorbance and PL effect were remaining after dividing pyrazoline dye to nanoparticles and bleaching by focused IR laser light. Fig. 9 shows that change of $I_{PL}(I_{pump})$ input-output characteristic did not cause significant change of two-photon PL effect criteria coefficient.

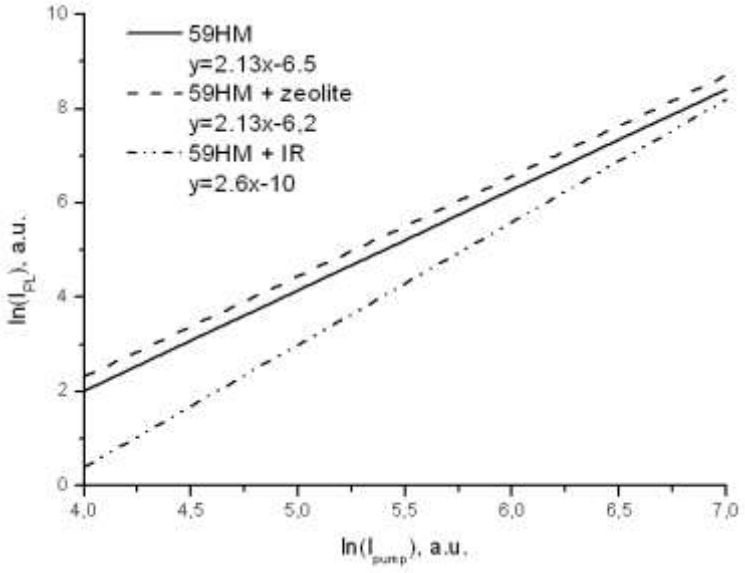

Fig. 9 Quadratic dependence of PL intensity from excitation intensity for pure, nanostructured and bleached samples of pyrazoline dye 59HM (logarithmic scale)

IV. CONCLUSIONS

The photoluminescent multilayer disc readout system, where readout signal is distinguished from parasitic as a variable one, was developed. It was shown that the thickness of disc intermediate layer must be big enough (50 μm or more) to make the parasitic signal stable, and information should be coded only by land's length to decrease absorption level of the information layer. It was proposed to build at information layer of PMD inner and outside peripheral areas that uphold a stable level of parasitic signal during readout from the edges of the disc.

It was shown that most of pyrazoline dyes could be accepted as effective registration media with a high quantum yield of PL, sufficient relaxation time, wide spectrum of the PL and possibility of two-photon absorption. Nevertheless, there is potential of the significant characteristic improvement based on the performance of organic dye molecules in the white zeolite matrix with additional laser annealing.

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