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NEAR IR LASER LIGHT VISUALIZATORS USING NONLINEAR GaSe AND OTHER LAYERED CRYSTALLITES

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Two methods of preparation of the devices for visualization of pulsed and continious near-IR (near infrared) are descrived and the results of conversion of pulsed and continuous IR (800-1360 nm) laser radiation into the visible range of spectra (400-680 nm) by using a transparent substrate covered with the particles (including nanoparticles) of effective nonlinear materials of $GaSe_xS_{1-x}$ ($0.2 \le x \le 0.8$) are presented. Converted light can be detected in transmission or reflectionn geometry as a visible spot corresponding to the real size of the incident laser beam. Developed device structures can be used for checking if the laser is working or not, for optical adjustment, for visualization of distribution of laser radiation over the cross of the beam and for invetsigation of the content of the laser radiation. Low energy (power density) limit for visualization of the IR laser pulses with 2 -3 *ps* duration for these device structures are: between 4.6 – 2.1 μJ ($3\cdot10^{-4}$ – $1\cdot10^{-4}$ W/cm^2) at 1200 *nm*; between 8.4 – 2.6 μJ ($4.7\cdot10^{-4}$ – $1.5\cdot10^{-4}$ W/cm^2) at 1300 *nm*; between 14.4 – 8.1 μJ ($8.2\cdot10^{-4}$ – $4.6\cdot10^{-4}$ W/cm^2) at 1360 *nm*. Threshold damage density is more than 10 MW/cm^2 at $\lambda = 1060$ *nm*, pulse duration $\tau = 35$ *ps*. The results are compared with commercially existing laser light visualizators.

1. INTRODUCTION

Near IR alser light converters are essential components in optical communication systems. These devices should have low power density limit (high energy sensitivity), high threshold damage, linear response and longer spectral sensitivity. Two types of converters are in use for visualization of the near IR radiation. Firts type is a commercial beam detector plates of KDP [$KH(PO_4)_2$-potassium dihydrogen phosphate], KTP [$KTiOPO_4$-potassium titanium phosphate] or seramic ABO_3 [eg. PZT, $Pb_x(Zr_{0.53}Ti_{0.47})O_3$. They consist of pressed microcrystals (fine powder) of KDP, KTP or PZT in a crystalline form. In this type of devices the seconf harmonic geneartion (SHG) effect is used for visualization. Second type of converters (IR laser sensors) are commercially distributed by LASER 2000 [2] and consist of a special phosphor material (different materials for wavelength from 250 nm to 1800 nm; standard from 750 to 1300 nm) burried in a plastic foil. In tehse type of devices a fine powder (microcrystals) in a crystalline form is burried in a plastic foil. The physical principle of light conversion is different in the second type of devices and based on the phosphorescence phenomenon.

Both type of these converters reveal strong and weak points. Among them are:

- first type permits to visualize the distribution of the intensity of laser radiation over the cross section of laser beam and to investifate a content of laser radiation. The sensitivity is limited, they do no give a possibility to visualize a weak radiation (less than 40 μJ power in a 1/e beam diameter of 1.5 mm) at 1053 nm and radiation at wavelength more or equal to 1200 nm.
- second type, in comparison with the first type, permits to visualize the alser radiation at 1053 nm and also at wavelength up to 1800 nm. The response isi highly nonlinear, they do not give the real spot size of the laser beam due of fluorescence of the regions of material which are close to the excited spot region. Besides this, the second type of converters do not givea possibility for visualization of distribution of the intensity of radiation over the cross section of laser beam and for investigation of content of laser radiation. Futhemore the seconf type of converters must be charged by a short exposure to a daylight or fluorescent light prior to use. The sensitivity decreases after exposure as a function of time.

All the above-mentioned, attracted our attention to the class of crystals with GaSe- type structure. It is well known, that highly anisotropic GaSe (chemical family – metal selenide, including GaS, InSe, GaTe) and $GaSe_xS_{1-x}$ ($0.2 \le x \le 0.8$) semiconductors posses several outstanding physical properties, the best known of which is a very high non-linear susceptibility $\chi(2)$ and a wide optical transmission range that is used for phase-matched second harmonic generation in a middle-IR and THz range of spectra [3 and references therein]. The optical band gap of this class of crystals is well suited for invetsigations with available lasers and is also convenient for testing the spectral response of the detection system (optical band gap for GaSe (red color) is $\Delta E = 2.02$ eV at room temperature (RT), for GaS (yellow) $\Delta E \approx 2.9$ eV (RT)).

$\chi(2)$ is mostly expressed in the ε-GaSe polytype, which belongs to non-centrosymmetric space group D_{3h}^1 [3]. This polytype is predominantly obtained by crystal growth from the melt and is used in our research. Other modifications, such as γ-GaSe and δ-GaSe are typically present as inclusions in grown crystals and exist as extended stacking faults in the layer plane (across to crystal **c**-axis which coincides with the dierction of crystallographic ***z***- axis).

The aim of the present research was to overcome negative sides of existing types of laser light converters by using only one device. To achieve the aim, we developed the method of preparation and investigated the properties of laser radiation converters which permit to visualize continuous and pulsed laser radiation in the spectral range from 900 nm to 1300 nm. As a basic material for converters we used GaSe and GaSe-GaS solid solutions.

2. METHOD OF PREPARATION, DATA PERFORMANCE, RESULTS AND DISCUSSION

All measurements were carried out with the crystals grown by the Bridgman method. The detailes of preparation of device structures was described in Ref. [4]. In addition to that given in Ref. [4], in the present work we describe also the method of preparation based by using the nanoparticles of nonlinear materials. Briefly these three methods are as follows:

Method A: **1. P**reparation of microcrystals (fine powder) which can be obtained by hand or mechanical grinding of poly- or single crystalline material in agate or any other morthar; **2.** Preparation of colloidal suspension of fine powder (microcrystals) in any liquids, which do not have chemical interaction with the materials (for example for class of materials studied in the present work it may be: water, methanol, ethanol, acetone, octan, hexan and other liquids); **3.** Mixing the colloidal suspension with any mixer; **4.** Putting some drops of suspension onto the surface of substrate up to the full covering the surface of substrate; **5.** Drying the substrate with coverage; **6.** Covering the surface of substrate containing microcrytals (fine powder) with any plastic foil solved in corresponding solvent (the foil should be optically transparent at least in the 450– 1360 nm range); **7.** Drying the device structure covered with plastic foil in air, under vacuum or inert atmosphere.

Method B: In principle the converters can be also made by preparation of colloidal suspension of microcrystals in any polymers (plastics) solved in corresponding solvent.

As one can see there are not too much differences between these two methods. In devices prepared by Method B the microcrystals (fine powder) are embedded in polymer (plastic) matrix, whereas in the devices prepared by Method A the microcrystals (fine powder) are covered with polymer (plastic) film.

Method C: We prepared converters also by fabrication of nanoparticles onto the substrate by laser ablation with KrF excimer laser. In this case the size of dots was successfully controlled: by the selection of experimental parameters of rare gas pressure; gas species of Ar or He; power of the laser pulse, and also the distance between the target and the substrate. The size distribution was studied: by TEM measurement (JEOL - JEM100C) and scanning SEM (JSM - 840) microscopes, the experimental results of the optical absorption (Perkin Elmer Lambda9 farting spectrometer), Raman scattering (home made confocal microspectrometer, He-Ne 632.8 nm line, 16 mWt) and infrared absorption (IR Fourier transform spectrometers (Perkin Elmer Spectrum 1 FTIR and Bomem DA-3). Not going too deep into the detaile of nano- particle formation and analysis of their optical properties we can summurize: **a)** size of the nano particles becomes larger with the increase of the rear gas pressure, and the size distributes wide with the increase of rare gas pressure; **b)** absorption edge shift with size is interpreted by the weak confinement effect on GaSe (also in the solid solutions of GaSe-GaS) Wannier-Mott type exciton taking into account the anisotropy of interlayer and intralayer forces; **c)** Raman scattering spectra of nano particles are analyzed with the Campbell-Fauchet analysis for the phonon confinement [5] taking into account the anisotropy of interlayer and intralayer forces. From the low frequency Raman data, decrease of the force constants of ca. 15% due to the formation of the nano dots are estimated.

It is worth to mention, that the conversion characteristics fo the devices prepared by all three methods are nearly the same.

Two kind of experimens were performed to invetsigate conversion characteristics of thin crystalline microcrystals (fine powder) in devices prepared by above mentioned three methods (hereinafter we will discuss the results obtained on GaSe).

First, the second harmonic conversion of laser radiation from 1053 nm up to 1400 nm was examined. The results were compared with a commercial beam detector plate of KDP.

Second, the second harmonic effeciency of our devices was examined in a transmission experiment.

As a laser source we used Nd:glass laser system with the followinf parameters: laser wavelength – 1053 nm; pulse duration – 2-3 ps; single pulse energy – 1.37 mJ; 1/e beam diameter – 1 mm.

A travelling wave dye laser was used as tunable light source with the next parameters: wavelength range: 1200 – 1400 nm; pulse duration: 3 ps; single pulse energy: 18 μJ (at 1200 nm); beam diameter: ca. 1 mm.

All energy measurements were made with a pyroelectric detector with an accuracy of typical ± 10 %.

Examination at 1053 nm: SHG efficiency was examined as a function of the energy of the incident laser pulse (69, 38, 26 and 12 μJ). The detection of the second harmonic converted signal was made visually. Our devices were examined in comparison with commercially existed plate of KDP converter.

At pulse energy ≤ 69 μJ commercially available plates showed weak second harmonic signal, whereas our devices showed already well noticeable green signal. Moreover, commercial plates do not convert the laser light at 1053 nm wavelength with energies less or equal 40 μJ, whereas the low energy limit for our converters was about 12 μJ. This result is expected taking into account the fact that nonlinear constant (determines the efficiency of the SHG signal) of GaSe is about $d_{22} = 72 \pm 6$ pm/V was determined at 1579 nm [6], whereas for KDP it is only about 0.5 pm/V [1]. Moreover, our converters allow to detect converted signal not only in reflection geometry, as in case of commercial plates, but also in the transmission geometry, which is very useful, for example, for optical allignment.

Examination between 1200 and 1400 nm: were made at: 1200 nm (18, 8.3, 4.6 and 2.1 μJ pulse energy); 1300 nm (26.8, 8.4 and 2.6 μJ pulse energy); 1340 nm (21.4 μJ); 1360 nm (14.4 μJ); 1380 nm (8.1 μJ) and 1400 nm (4.3 μJ).

No converted signal was observed with commercial KDP plates at wavelength of the incident laser pulses of more than or equal to 1200 nm. At the same time, our devices permitted to visualize the laser pulses up to the wavelength 1360 nm. Low energy limit for visualization of the IR laser pulses using our devices were: between 4.6 – 2.1 μJ at 1200 nm; 8.4 – 2.6 μJ at 1300 nm and 14.4 – 8.1 μJ at 1360 nm.

Conversion efficiency: the IR (1053 nm) and second harmonic (526.5 nm) intensity was measured with an avalance diode (high voltage 1.3 kV). IR signal pulse energy was 1.37 mJ. The measurements were performed according to the following experimental setup as follows:

IR laser beam → Visualizator → Second Harmonic Signal → IR Blocking Filter → Avalance Diode

A conversion efficiency (number of photons as the second harmonic devided by the number of photons at incident IR laser light) of about 10^{-7} was obtained.

3. CONCLUSIONS

New type of visualizators for conversion of pulsed and continuous IR (900 - 1360 nm) laser radiation into the visible

range (450 – 680 nm) of spectra are suggested. Device consists of the crystallites of GaSe- type semiconductor materials embedded into the transparent matrix and covered onto the surface of glass (or any other transparent) plate. It can be used in reflection as well as in transmission geometries. The visualizators are based on the GaSe and GaSe-GaS solid solutions and may be used for checking if the laser is working or not, for optical adjustment, for visualization of distribution of the intensity of laser radiation over the cross of the beam and for investigation of the content of the laser radiation. Specifications for suggested devices are as follows: visualizator gives integral lightness in the green range of spectra (526 – 527 nm) when excited with 2 – 3 ps laser pulses (λ = 1053 nm) with a power density of excitation of $7 \cdot 10^{-4}$ W/cm^2 (12 μJ, 1/e beam diameter 1.5 mm). Low-energy power density limit for visualization of the IR laser pulses with 2 – 3 ps duartion for these devices are: between 4.6 – 2.1 μJ ($3 \cdot 10^{-4}$ – $1 \cdot 10^{-4}$ W/cm^2 at 1200 nm; between 8.4 – 2.6 μJ ($4.7 \cdot 10^{-4}$ – $1.5 \cdot 10^{-4}$ W/cm^2) at 1300 nm; between 14.4 – 8.1 μJ ($8.2 \cdot 10^{-4}$ – $4.6 \cdot 10^{-4}$ W/cm^2) at 1360 nm. Threshold damage density is more than 10 MW/cm^2 at λ = 1060 nm, pulse duration τ = 35 ps.

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