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GaInSn liquid nanospheres as a saturable absorber for Q-switched pulse generation at 639 nm

Bo Chen, Peifu Wang, Ning Zhang, Kuan Li, Ke Zhang, Shande Liu, Jinlong Xu, and Zhipei Sun

Abstract: Liquid metals, which possess the superiority of low cost, shape-reconfigurability, and excellent optoelectronic properties, have been applied in various fields, such as flexible electronics, superconductivity, and coolants. In this paper, high-quality GaInSn liquid nanospheres synthesized by the ultrasonic method are applied for nonlinear optics and laser switches. The saturation absorption property derived from localized surface plasmon resonance at 639 nm is studied based on the open-aperture Z-scan technique, exhibiting a modulation depth of ∼35.5% and a saturation fluence of ∼21.75 mJ/cm², respectively. The as-prepared GaInSn liquid nanospheres are also successfully utilized as a saturable absorber to achieve a stable Q-switched Pr:YLF laser at 639 nm. The output pulse width can reach ∼280 ns with a pulse repetition rate of ∼174.8 kHz. Our results suggest that GaInSn liquid nanospheres are a candidate material for generating visible laser pulses, which is of great interest for potential applications in visible nonlinear optics.

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1. Introduction

In the past decade, pulsed visible lasers have been developed rapidly owing to their unique applications in bio-optics, medical therapy, and underwater laser communication, etc [1–4]. Compared with the nonlinear frequency conversion method, lasers achieved by the two-dimension materials as saturable absorbers have advantages of low cost, easy fabrication, compactness, and designability [5–9]. Analogously, the strong interaction between surface plasmon resonance and electric field of the metallic nanomaterials contributes to its remarkably optical properties, making them excellent optical switches in the visible waveband [10,11]. Indeed, many efforts have been paid to explore the nonlinear saturation absorption properties and their laser applications of various metallic nanomaterials. For example, K.-H. Kim et al. demonstrated an ultrafast nonlinear optical response of Au nanoparticles with the pump-probe technique, showing a short response time of 1.6 ps [12]. In 2015, high-quality Au nanorods were synthesized and successfully utilized in Pr:YLF bulk lasers operating at orange, red, and deep red spectral regions [13]. This distinction was further conducted by Wu et al. in a Pr³⁺-doped ZBLAN fiber laser generating a pulse width as shortest as 235 ns [14]. Although Au nanomaterials have presented significant properties and satisfied laser application requirements, they are found to be expensive.

More recently, a novel liquid metal nanomaterial, GaInSn, has caught great attention for its excellent properties in various domains such as mechanical actuation, wearable electronics, and cooling of various precision instruments [15–17]. Nevertheless, few studies on its nonlinear...
optical property were presented. Similar to the characteristics of most zero-dimensional materials, the nonlinear optical properties of GaInSn nanospheres are governed by the excitation of localized surface plasmon resonance (LSPR) as well [18]. It refers to the strong interaction between surface plasma and the incident laser’s electric field, which causes polarizability’s intensity and outstanding optical characteristics. The amorphous and high ductility of the liquid metal nanomaterials result in plasmonic microcavities of diverse sizes, exhibiting a broader LSPR than those of traditional nanoparticle materials. In order to explore their linear and nonlinear optical effect, some researchers have fabricated liquid metals and applied them in pulsed lasers. For instance, Q-switched lasers using GaInSn nanospheres as a saturable absorber (SA) were both successfully realized at ∼1.3 µm and ∼2 µm, respectively, demonstrating a pulse width of ∼32 ns at ∼1.3 µm and that of ∼510 ns at ∼2 µm [18]. Noting that the strongly enhanced LSPR of metal nanoparticles at optical frequencies makes them perfect absorbers and scatterers of visible light [19–21], which indicate that they could be an ideal SA candidate for optical switches or mode-lockers in the visible wavelength. Therefore, the nonlinear optical properties, including its performance as SAs in visible pulse lasers, need further research.

Herein, high-quality GaInSn liquid nanospheres were synthesized by the ultrasonic method. The saturation absorption property of the as-prepared GaInSn nanospheres at 639 nm was measured through the open-aperture Z-scan technique, presenting a modulation depth of ∼35.5% and a saturation fluence of ∼21.75 mJ/cm², respectively. After, we used the GaInSn liquid nanospheres based SA for visible ultrafast pulse generation at 639 nm. The shortest pulse width of ∼280 ns with a maximum repetition rate of ∼174.8 kHz was obtained.

2. Characterization of liquid metal GaInSn nanospheres

We utilized the ultrasonic method to fabricate GaInSn nanospheres for the weak bonding force between liquid metal atoms. The fabrication process can be briefly described as follows. First, the three metals were mixed in the proportions of 68.5% Ga, 21.5% In, and 10% Sn and heated for 10 min at 350 °C to form a GaInSn alloy. As shown in Fig. 1(a), the as-prepared liquid GaInSn alloy was stored in the vessel. To comminute it into nanospheres, the GaInSn alloy was subjected to ultrasonic in acetone for about 20 h. The GaInSn nanospheres with nanometer diameter and uniform shape could be received by optimizing the ultrasonic process parameters and multiple precipitations. As described in Fig. 1(b), the morphology of the GaInSn nanospheres was characterized by a scanning electron microscope (SEM). To observe the shape and size of the nanospheres more clearly, a transmission electron microscope (TEM) was applied, and the morphology was displayed in Fig. 1(c). The TEM image showed that the as-prepared GaInSn nanospheres were almost uniformly spherical, and the corresponding size distribution was illustrated in Fig. 1(d).

Furthermore, the open-aperture Z-scan technique was employed to explore the nonlinear saturation absorption property of the as-prepared GaInSn nanospheres at 639 nm. The laser source was a femtosecond laser with a pulse duration of ∼120 fs and a repetition rate of 5 kHz, respectively. Figure 2(a) displays a measurement result of the normalized nonlinear transmittance at 639 nm. The transmittance increased with the incident laser intensity exhibiting a strong saturation behavior of the GaInSn liquid nanospheres. Generally, the nonlinear transmittance can be written as the following formula:

\[
T(z) = \sum_{n=0}^{\infty} \left( -\beta_{\text{eff}} L_{\text{eff}} I_0 \right)^n /(1 + \frac{Z^2}{Z_0^2})^n (n + 1)^{3/2} \\
\approx 1 - \frac{\beta_{\text{eff}} L_{\text{eff}} I_0}{2^{3/2}} (1 + \frac{Z^2}{Z_0^2})
\]
Fig. 1. (a) GaInSn liquid alloy stored in the vessel. (b) SEM image. (c) TEM image. (d) Corresponding size distribution, the nanosphere number in Panel d is labeled in Panel c.

Fig. 2. (a) Open aperture Z-scan curve of the GaInSn nanospheres. (b) Normalized nonlinear transmittance versus the pump laser fluence.
where $Z_0$, $I_0$, $\beta_{\text{eff}}$, and $L_{\text{eff}}$ are Rayleigh length, on-axis peak intensity, the effective nonlinear absorption coefficient, and the thickness of the GaInSn nanospheres sample, separately. The effective nonlinear absorption coefficient $\beta_{\text{eff}}$ was fitting to be $-3.09 \times 10^{-2} \text{ cm/GW}$, which was two-time larger than that of black phosphorus nanosheets and graphene at 800 nm [22,23]. Additionally, the saturation absorption curve was fitted by the following formula:

$$T(I) = 1 - \frac{\Delta R}{1 + I/I_s} - A_{\text{ns}}$$

(2)

where $I_s$, $\Delta R$, and $A_{\text{ns}}$ represent saturable fluence, modulation depth, and non-saturable loss. Figure 2(b) demonstrates the saturation fluence of $\sim 21.75 \text{ mJ/cm}^2$ and the modulation depth of $\sim 35.5\%$, respectively, which indicate excellent saturation absorption characteristics of the GaInSn liquid nanospheres.

3. Experimental setup

Figure 3 shows the schematic diagram of the GaInSn nanospheres Q-switched laser. A $3 \times 3 \times 5 \text{ mm}^3$ Pr:YLF crystal with a doped concentration of 0.5 at.% was selected as the gain medium, and both end surfaces of the crystal were polished adequately. To reduce the thermal lensing effect, the crystal was wrapped with an indium foil and mounted in a copper with the temperature-controlled at $\sim 12.3 \text{ °C}$. The pump source was a fiber-coupled GaN blue laser diode (LD) with a central wavelength of 442 nm and a core diameter of 200 $\mu\text{m}$. The pump light from the LD is focused on the crystal through a planoconvex lens with a focal length of 50 mm. The input mirror (IM) was a plano-plane mirror with anti-reflection coated at 442 nm and high reflection coated at 639 nm. The output couplers (OCs) had a curvature radius of $R = 50 \text{ mm}$ at different transmittances at 639 nm (0.5%, 1.5%, and 5% are available). Furthermore, to remove the undepleted pump light, an optical filter was put behind the OCs.

![Fig. 3. Schematic setup of the GaInSn nanospheres Q-switched laser.](image)

By using OCs with different transmittances, the continuous-wave (CW) laser operation was demonstrated first. The absorption efficiency of the 0.5 at.% Pr:YLF crystal at 442 nm was measured to be about 80.5% to calculate the absorbed pump power in our measurement. Figure 4(a) demonstrates the average output powers with the absorbed pump power at different transmittances under the CW laser operation. Under the maximum absorbed pump power of $\sim 3.6 \text{ W}$, a maximum average output power of $\sim 730 \text{ mW}$ with a slope efficiency of 26.9% was achieved when we used the OC with the output transmittance of 5%.

To explore the saturation absorption property of the GaInSn nanospheres for pulse generation at 639 nm, the as-prepared GaInSn nanosphere-based SA was inserted into the laser cavity and placed closely behind the Pr:YLF crystal. After optimizing the cavity parameters, the passively Q-switched (PQS) laser was realized. As presented in Fig. 4(b), the output power of the
Q-switched laser increased monotonously with the absorbed pump power. The maximum output power was \( \sim 45.5 \text{ mW} \) under the maximum absorbed pump power of 3.6 W at the transmittance of \( T = 5\% \).

The laser output spectra of the CW and PQS operations are exhibited in Fig. 5. We typically observed laser oscillation at 2 different wavelengths: one is at 639 nm, and another one is at 720 nm. It was obvious that the mode oscillation intensity of the 720 nm tended to weaken in the PQS laser for \( T = 0.5\% \). This can be explained as follows. The transmittance at 720 nm of the above-mentioned OC was 1.2\%. Therefore, the output intensity at 720 nm is higher than that at 639 nm owing to the higher transmittance at 720 nm. When the GaInSn nanosphere-based SA was inserted into the laser cavity, the cavity loss at 720 nm increased. The laser mode of 639 nm was at a superior position in the mode comparison with 720 nm owing to its larger emission cross-section of the Pr:YLF crystal (\( \sigma_{639 \text{ nm}} = 2.18 \times 10^{-19} \text{ cm}^2; \sigma_{720 \text{ nm}} = 8.8 \times 10^{-20} \text{ cm}^2 \)).

The laser pulse characteristics were detected by a Si detector (DET025A/M, 2 GHz bandwidth, 400 to 1100 nm wavelength range) and synchronously displayed on a digital oscilloscope (RTO 2012, 1 GHz bandwidth, 10 Gs s\(^{-1}\) sampling rates). Figures 6(a), 6(b), and 6(c) depict the pulse durations and repetition rates versus the absorbed pump power at different transmittances of the OCs, respectively. With the transmittance of \( T = 0.5\% \), the pulse repetition rate increased almost linearly from \( \sim 123.3 \) to 174.8 kHz, while the pulse duration decreased from 480 ns to 280 ns. The shortest pulse duration of 280 ns and the maximum repetition frequency of \( \sim 174.8 \text{ kHz} \) were achieved. When transmittance of \( T = 5\% \) was used, the pulse width varied from \( \sim 560 \) to 360 ns,
and the repetition rates presented the variations of \( \sim 79.87-121.9 \) kHz with the increase of the absorbed pump power from \( \sim 2.2 \) to \( 3.6 \) W.

Fig. 6. The pulse width and repetition rate of the PQS laser versus the absorbed pump power at (a) \( T = 0.5\% \), (b) \( T = 1.5\% \), (c) \( T = 5\% \); the dependence of pulse energy and peak power on the absorbed pump power at (d) \( T = 0.5\% \), (e) \( T = 1.5\% \), (f) \( T = 5\% \).

According to the equations of \( E = P_A/f \) and \( P_P = E/t \), where \( P_A \), \( f \), and \( t \) were separately average output power, repetition rate, and pulse width, the single pulse energy (\( E \)) and peak power (\( P_P \)) could be calculated. The pulse energy and peak power as a function of the absorbed pump power were recorded at \( T = 0.5\% \), 1.5\%, and 5\% transmittances are shown in Fig. 6(d), 6(e), and 6(f). Under the maximum absorbed pump power of 3.6 W, the maximum single pulse energy was 74.9 nJ at \( T = 0.5\% \), 88.2 nJ at \( T = 1.5\% \), and 373.3 nJ at \( T = 5\% \), respectively, corresponding to the maximum peak power were 267.7 mW, 314.9 mW, and 1036.8 mW. Figure 7 demonstrates the typical single pulse profile and temporal pulse trains indicating a stable operation of the PQS laser.
Fig. 7. Typical pulse trains and single pulse profiles of the PQS laser at (a) $T = 0.5\%$, (b) $T = 1.5\%$, (c) $T = 5\%$.

4. Conclusion

In conclusion, high-quality GaInSn liquid nanospheres were successfully fabricated by the ultrasonic method. The nonlinear optical property was explored through the open-aperture Z-scan technique, presenting a modulation depth of 35.5\% and a saturation fluence of $\sim 21.75$ mJ/cm$^2$ at 639 nm, respectively. The as-prepared GaInSn nanospheres were successfully applied as a saturable absorber to achieve a stable Q-switching Pr:YLF laser operation with the shortest pulse width of 280 ns and the highest pulse repetition rate of 174.8 kHz. The results of this work demonstrate the great potential of GaInSn nanospheres in visible nonlinear optics.

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Disclosures. There are no conflicts to declare.

Data availability. The data that support the plots and maps within this paper and other findings of this study are available from the corresponding authors upon reasonable request.

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