Hot-pressed ceramic Fe:ZnSe gain-switched laser

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Abstract: We report the first room temperature gain-switched Fe:ZnSe hot-pressed ceramic laser pumped by 2.94 \( \mu \)m radiation of mechanically Q-switched Er:YAG laser. The maximum output energy at 4.2 \( \mu \)m was 41 mJ at 3 Hz repetition rate and 120 ns pulse duration. The measured slope efficiency was 25% with respect to the absorbed energy. This technique could be attractive for the future development of high-energy short-pulse solid-state mid-IR systems.

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1. Introduction

Recently, many efforts have been devoted towards the development of affordable broadly tunable middle infrared (mid-IR) solid state laser sources operating in free-running, gain-switched (GS), and Q-switched regimes. These mid-IR lasers are essential for free-space optical communication, remote sensing of atmospheric constituents, laser radar (LIDAR), spectroscopy and numerous medical and defense related applications [1–3]. Iron doped ZnSe/ZnS crystals were proven to be materials of choice for lasers with direct access to the mid-wave infrared (3.5-8 \( \mu \)m) spectral range with promising energy scaling capability and realization of their potential requires strong effort in understanding physics of these materials and further optimization of fabrication technology [2,3]. So far, among these materials, the most significant results have been reported for Fe:ZnSe crystals due to their high gain cross section, broad 3.6-5.2 \( \mu \)m spectral coverage, and absence of excited state absorption [2]. The lifetime of the upper laser level 5\( T_2 \) of the Fe\(^{2+} \) ion in a ZnSe crystals decreases with temperature from \( \tau \approx 57 \) \( \mu \)s at 120 K to 380 ns at room temperature (RT) due to the nonradiative relaxation process [4]. It allows an effective laser operation at both RT and low temperature regimes. In continuous wave (CW) regime, output power up to 9.6 W was demonstrated from a Fe:ZnSe laser in a non-selective cavity at 77 K [5]. The first RT gain-switched Fe:ZnSe lasing was demonstrated under 2.92 \( \mu \)m excitation [6]. Recently, 1.43 J of output energy in 150 ns pulse with 53% slope efficiency from gain-switched Fe:ZnSe laser was demonstrated using hydrogen fluoride (HF) pump source [7]. However, the toxicity of this chemical HF pump laser limits its applications. An Er:YAG solid state laser can be used as a convenient pump source for a Fe:ZnSe laser, since 2.94 \( \mu \)m Er:YAG output nicely overlaps with the absorption band of Fe\(^{2+} \) ions in II-VI materials. In 2018, the Fe:ZnSe laser with output energy up to 7.5 J and 30% slope efficiency in a single-shot operation at 4.3 \( \mu \)m pumped by free-running radiation of Er:YAG laser was reported [8]. Due to temperature quenching of the upper laser level, free running operation of a Fe:ZnSe laser requires cooling of the gain element to at least \( \sim \) 220 K. The effective RT operation of Fe:ZnSe laser requires pump pulses to be shorter than the upper laser level lifetime (380 ns) [6,9]. At RT, gain switched Fe:ZnSe laser with 5 mJ of output energy under 15 mJ (150 ns) of Er:YAG pump energy was reported [10].

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The fabrication of high-quality Fe:ZnSe crystals is a challenging task. Currently, one of the most common Fe:ZnSe gain elements fabrication method is based on chemical or physical vapor transport growth of polycrystalline ZnSe followed by post-growth thermal diffusion of iron. However, due to the relatively small coefficient of Fe$^{2+}$ ions diffusion in ZnSe ($D = \text{3.7} \times 10^{-10}$ cm$^2$/s at 950°C [11]), this approach limits the fabrication of large size, homogenously doped Fe:ZnSe crystals. On the other hand, hot-pressing ceramic method has great potential to overcome these limitations. In 1966, hot-pressed CaF$_2$ doped dysprosium was reported as the first ceramic laser material [12]. In 2009, output power up to 100 kW was demonstrated from Nd:YAG ceramic laser [13]. In recent years, there has been a development on transition metal doped II-VI chalcogenide ceramic samples prepared mostly by using hot-pressed technique. In 2006, first Cr:ZnSe ceramic sample was prepared by hot pressing ZnSe and CrSe powders [14]. This result was a milestone for the future development of mid-IR transparent ceramics for laser applications. After that, in 2016, hot-pressed Cr:ZnS [15] and in 2017 [16], hot-pressed and post hot isostatic press (HIP) treated Fe:ZnS ceramic samples were prepared with 40% and 67% transmissions at lasing wavelengths, respectively. Finally, in 2019, first hot-pressed Fe:ZnS ceramic sample was prepared with 25% transmission at 4.5 µm [17]. Among these mid-IR transparent ceramics, the laser oscillation has been demonstrated only with Cr:ZnSe gain element.

In this paper, we report on development of the first RT gain-switched laser oscillation of hot-pressed ceramic Fe:ZnSe laser pumped by radiation of 2.94 µm mechanically Q-switched (MQS) Er:YAG laser. The objective of this study is to demonstrate that the hot-pressed ceramic technology is a promising pathway for fabrication of large-scale, uniformly doped mid-IR Fe:ZnSe gain media. This emerging technology has an excellent potential to prepare laser gain media for the future low cost, compact, and high-power mid-IR laser applications.

2. Sample preparation

The preparation of hot-pressed Fe:ZnSe ceramic sample was a multi-step process involving powder preparation, and multi-step pressing and heating procedures. First, for the synthesis of Se$^{2-}$ solution, transparent NaHSe solution was prepared in which NaH$\cdot$B was dissolved in deionized water with stoichiometric amount of Se (99.5%, Sigma-Aldrich). Then transparent NaHSe solution was mixed with stoichiometric amount of FeCl$_2$·4H$_2$O (99.0%, Sigma-Aldrich) and ZnCl$_2$ (99.0%, Sigma-Aldrich) to obtain Fe:ZnSe nanopowders. By using centrifugation technique, resulting precipitants were separated and washed with ethyl alcohol and then dried for 24 hours in argon at 80°C. The dried precipitant was then ground in an agate mortar and calcinated at 400°C for 6 hours. Finally, these nano-powders were sintered by Spark Plasma Sintering (SPS) technique at 900°C in vacuum under 90 MPa pressure for 20-120 minutes as described in details in [18]. With this technique, four different Fe:ZnSe ceramic samples were prepared with different dopant concentrations (from 0.5% to 3%) of ferrous chloride during fabrication process. The photos of these samples are shown in Fig. 1.

Fig. 1. Photos of four different hot-pressed Fe:ZnSe ceramic samples with different dopant concentrations of ferrous chloride used during fabrication process.
3. Experimental results and discussion

Figure 2(a) shows the transmission spectra of four different Fe:ZnSe ceramic samples with four different dopant concentrations of Fe$^{2+}$ ions measured using a Fourier-transform infrared (FTIR) spectrometer Shimadzu IRAffinity. Strong absorption band near 3 µm results from $5E\rightarrow5T_2$ transition of Fe$^{2+}$ ions. The concentrations of Fe$^{2+}$ ions in each sample were calculated using a well-documented absorption cross-section value $\sigma=1.0 \times 10^{-18}$ cm$^2$ at 3.1 µm [2]. The calculated Fe$^{2+}$ concentrations of four samples represented by curves I, II, III, and IV, as shown in Fig. 2(a), were $1.4 \times 10^{18}$, $2.9 \times 10^{18}$, $6.2 \times 10^{18}$, and $9.0 \times 10^{18}$ cm$^{-3}$, respectively. It is noteworthy that the low doped Fe:ZnSe ceramics samples I and II featured conductivity of ~0.2 S/m accompanied by a characteristic increase of IR losses with wavelength associated with light absorption by carriers. Figure 2(b) shows the linear relationship between the initial iron concentration used in the fabrication process and the final concentration of Fe$^{2+}$ ions in samples calculated from FTIR measurements with slope 3. We believe that the difference between the initial iron concentration in solution and the final concentration in ceramics is due to the different Fe segregation coefficients in ceramic green body and solution. In our current work, we used 3.2 mm thick Fe:ZnSe ceramic sample with iron concentration $\sim 9 \times 10^{18}$ cm$^{-3}$. At RT, the measured active absorption of this 3.2 mm sample was 91% at the pump wavelength.

![Fig. 2.](image)

**Fig. 2.** (a) Transmission spectra of 4 different hot-pressed Fe:ZnSe samples with different iron concentrations ($N_{Fe}$: $1.4 \times 10^{18}$, $2.9 \times 10^{18}$, $6.2 \times 10^{18}$, $9.0 \times 10^{18}$ cm$^{-3}$ for curve I, II, III, and IV, respectively); (b) Relation between concentration of Fe$^{2+}$ ions in Fe:ZnSe ceramics and ferrous chloride used in the fabrication process.

Figure 3(a) demonstrates RT kinetics of luminescence lifetime measurement at $5E\rightarrow5T_2$ transition of Fe:ZnSe ceramic and polycrystalline samples under 2.94 µm pumping. The non-selective photoluminescence after long-pass IR filter with 3500 nm cutoff wavelength was collected by CaF$_2$ lens and measured by HgCdTe detector with temporal response faster than 1.2 ns. For this measurement, samples with similar concentrations of Fe$^{2+}$ ions ($\sim 9.0 \times 10^{18}$ cm$^{-3}$) were used. As one can see from the Fig. 3(a), both Fe:ZnSe samples reveal single exponential decay with $\sim 220$ ns time constant. These measurements show that the luminescence lifetime of the hot-pressed Fe:ZnSe ceramic sample is in a good agreement with that of the lifetime of conventionally thermally diffused Fe:ZnSe polycrystalline sample. This implies that the active centers in both ceramic and polycrystalline samples have similar optical properties. We believe that the decay times in studied samples were smaller than that previously reported in [4] due to the concentration quenching in highly doped samples, however, specific mechanism of this quenching is still under study. The uncalibrated photoluminescence spectrum of Fe:ZnSe ceramic sample covering the spectral range over 3500-5500 nm is shown in Fig. 3(b) (curve I).
During the measurement, we used a mid-IR filter with a cutoff wavelength at 3500 nm to block the pump radiation. The dip at $\sim 4250$ nm results from atmospheric CO$_2$ absorption.

![Graph](image)

**Fig. 3.** (a) Luminescence lifetime measurement of Fe:ZnSe ceramic (curve I) and polycrystalline samples (curve II), (b) Photoluminescence spectrum (curve I) of hot-pressed Fe:ZnSe ceramic sample (not calibrated to the spectral sensitivity of detection platform) and spectrum of laser oscillation (curve II).

For the laser experiment, since the 2.94 $\mu$m oscillation wavelength nicely overlaps with the absorption band of Fe$^{2+}$ ions in II-VI materials, the 2.94 $\mu$m radiation of a home-made MQS Er:YAG laser operating at 3 Hz [10,19] was utilized as a pump source for Fe:ZnSe ceramic laser. We used a non-selective linear cavity (20 mm long) containing CaF$_2$ based flat dichroic high reflector (DM) and output coupler with 70% reflectivity, as well as 3.2 mm thick Fe:ZnSe ceramic crystal having $9.0 \times 10^{18}$ cm$^{-3}$ Fe$^{2+}$ concentration with uncoated facets clamped between two copper plates at RT. The pumping was done both collinearly and quasi-collinearly with respect to the resonator axis as shown in Fig. 4(a) and (b). A CaF$_2$ lens (F1) with 25 cm focal length was used to focus the pump beam at the Fe:ZnSe sample to a 2 mm diameter spot. The diameter of the pump beam on the focusing lens was estimated using energy passing through a variable IRIS aperture. The diameter of the pump beam on the active element was calculated based on the known beam diameter at the lens, its focal length and the distance between the lens and the gain element. The calculated value was close to the spot diameter measured with the use of thermal paper. We have measured the spot size of the laser mode near the output coupler and it was close to the pump spot at the facet of the gain element. So, the spatial overlap of the laser mode and the pumping beam was reasonably good. The two dichroic mirrors (DM) having transmission $\sim 94\%$ at pump wavelength and a high reflectivity over 3.5-5.2 $\mu$m spectral range were used after output coupler to separate residual pump radiation and oscillation of the Fe:ZnSe laser. In order to direct the Fe:ZnSe laser radiation to the power meter, another focusing lens (F2) with focal length 15 cm was used. The measured Fe:ZnSe laser spectrum is shown in Fig. 3(b) (curve II). The Fe:ZnSe laser oscillation spectrum has maximum intensity at 4.21 $\mu$m and features a line narrowing with respect to PL to a linewidth of $\sim 50$ nm. The long-wavelength shift of the oscillation wavelength with respect to maximum of PL signal could be explained by Füchtbauer–Ladenburg relationship between gain and PL spectra.

The output-input characteristics of the hot-pressed Fe:ZnSe ceramic laser at two different pumping regimes are shown in Fig. 5. At collinear [Fig. 5(a) (inset graph)] and quasi-collinear pumping [Fig. 5(a) & (b)], the threshold energies of the Fe:ZnSe ceramic laser were measured to be 2 mJ and 3 mJ, respectively. The maximum output energies were measured to be 8 mJ and 41 mJ at collinear and quasi-collinear pumping, respectively. The slope efficiencies were measured to be 25% with respect to the absorbed pump energy at both pumping regimes. The absorbed
Fig. 4. Schematic diagram of gain-switched hot-pressed ceramics Fe:ZnSe laser at (a) collinear, and (b) quasi-collinear pumping regimes, where PM (power meter), DM (dichroic mirror), OC (output coupler), and F1 and F2 are the bi-convex lenses.

Energy was calculated by subtracting the measured residual pump energy and reflected energy from the front surface of the sample (calculated using Fresnel equation) from the incident pump energy.

Fig. 5. Output-input characteristics of the Fe:ZnSe hot-pressed ceramic laser at (a) collinear and quasi-collinear pumping for comparison at lower pump energies (inset plot), and (b) quasi-collinear pumping.

At collinear pumping, the maximum output energy was limited by the optical damage of Fe:ZnSe HR mirror. On the other hand, at quasi-collinear pumping, maximum output energy was limited by the available pump energy in a single pulse from MQS Er:YAG laser. In future, the output characteristics of this Fe:ZnSe ceramic laser are expected to be significantly improved with the reduction of scattering losses, use of HR mirror with higher damage threshold at pump wavelength (collinear pumping), and availability of higher pump energy in a single pulse (quasi-collinear pumping).

Figure 6(a) shows the temporal profiles of the pump and Fe:ZnSe laser pulses at 280 mJ pump and 41 mJ of output energies, respectively, measured under quasi-collinear pumping. The pulse
durations of pump and Fe:ZnSe lasers were 145 ns and 120 ns, respectively, which were measured with a fast Boston Electronics PEMI series HgCdTe detector with a response time of ∼1.2 ns. Figure 6(b) shows the typical beam profile of Fe:ZnSe ceramic laser at 41 mJ output energy measured by PyroCam III (Spiricon). As we can see from the figure, the beam profile does not feature any hot spots.

![Fig. 6.](image)

**Fig. 6.** (a) Temporal profiles of the pump and Fe:ZnSe laser, and (b) spatial beam profile of the Fe:ZnSe laser at 41 mJ of output energy.

### 4. Conclusions

In summary, we report the first RT gain-switched lasing of Fe:ZnSe hot-pressed ceramic sample pumped by 2.94 µm radiation of mechanically Q-switched Er:YAG laser operating at 3 Hz. In quasi-collinear pumping regime, the maximum output energy was measured to be 41 mJ with 120 ns pulse duration at FWHM. The measured slope efficiency with respect to the absorbed energy was 25%. The maximum output energy was limited by the pump energy in a single pulse at 3 Hz. In collinear pumping regime, the maximum output energy was measured to be 8 mJ with 25% slope efficiency with respect to the absorbed energy and limited by the optical damage of the input mirror. In future, output characteristics of the Fe:ZnSe ceramic laser are expected to be significantly improved with the reduction of scattering losses and availability of higher pump energy in a single pulse. The hot-pressed ceramic technique could be very appealing for the future development of high-energy short-pulse solid-state mid-IR laser systems.

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Disclosures

The authors declare that there are no conflicts of interest related to this article.

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