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Middle-infrared random lasing of Cr^{2+} doped ZnSe, ZnS, CdSe powders, powders imbedded in polymer liquid solutions, and polymer films

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ABSTRACT

Room temperature (RT) middle-infrared (Mid-IR) random lasing of chromium- (Cr) doped ZnSe, ZnS, and CdSe powders, powders imbedded in perfluorocarbon liquid polymer solutions, and fluorocarbon polymer films is reported. Laser active powders were prepared without a stage of bulk crystal growth by annealing of starting chemicals (pure, mixed ZnSe:CrSe; ZnS:CrS; CdSe:CrSe). Mixture of the different semiconductor hosts allows tuning oscillation wavelength from 2240 to 2630 nm.

1. Introduction

Random lasers are based on laser active scattering media without any cavity as well as other optical elements. The positive laser feedback arises due to photons scattering. The random lasers, having a low cost of fabrication [1], are useful for many applications, such as low coherence laser sources [2], X-ray lasers and γ-ray lasers [3], low-noise imaging, and new lighting systems [2]. Random lasing was first reported in an experimental study of neodymium doped powder [4]. Since then a variety of random lasers have been developed based on fine laser crystal powders [5–8], fine glass powders [9,10] and dye-doped polymers [11–13]. Most of these random lasers operated over visible to near-infrared range of optical spectrum. In the mid-90s there appeared a new class of mid-infrared (Mid-IR) laser materials: transition metal (TM)-doped zinc and cadmium chalcogenides [14]. These materials are characterized by close to 100% quantum efficiency of mid-IR fluorescence at room temperature (RT) and high $\sigma\tau$ (cross-section × lifetime) product resulting in an intrinsically low lasing threshold among other attractive spectroscopic features. The optically pumped Cr^{2+}-doped chalcogenide lasers offer a unique combination of efficient (up to 70% at RT) operation over 2–5 μm spectral range and ultra-broad gain bandwidth (up to 50% of central wavelength). Recently, an efficient Mid-IR lasing was demonstrated for bulk Cr^{2+}:ZnS [15], Cr^{2+}:ZnSe [16,17], Cr^{2+}:CdSe [18], and Fe^{2+}:ZnSe [19] crystals at RT.

First chromium-doped ZnSe and ZnS random powder lasers were demonstrated in [20–22]. In these papers, the powder samples were fabricated by a mechanical grinding of Cr:ZnSe and Cr:ZnS crystals. The reported [21] threshold pump energy density was about 20 mJ/cm^2 and ~30 mJ/cm^2 for ZnSe and ZnS powders, respectively.

In the current work, we report a simple method of Cr^{2+}-doped ZnS, mixed ZnS and ZnSe (1:1 wt%; ZnSSe), ZnSe and CdSe lasing powders fabrication without the crystal growth stage. The average grain size of the powders was around 10 μm. The basic spectroscopic properties of the prepared Cr^{2+}-doped ZnS, ZnSSe, ZnSe and CdSe powders (lasing around 2241, 2330, 2355 and 2632 nm, respectively) as well as liquid and polymer film laser active samples based on Cr-doped ZnS and ZnSe powders are presented. The powder, liquid, and polymer samples were

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characterized through the measurement of photoluminescence (PL) spectra, PL kinetics, and lasing threshold energy.

2. Samples fabrication

The fabrication of Cr^{2+}:ZnSe, Cr^{2+}:ZnS and Cr^{2+}:CdSe powders involved two simple stages. At the first stage pure ZnSe and CrSe, ZnS and CrS, or CdSe and CrSe chemicals having an average grain size of ~5–10 μm (with a chromium concentration of $5 \times 10^{19}\ cm^{-3}$, $2 \times 10^{19}\ cm^{-3}$, and $1 \times 10^{20}\ cm^{-3}$, respectively) were uniformly mixed with a mechanical shaker. At the second stage the obtained powders were sealed into an evacuated (10^{-4} Torr) quartz ampoules and annealed at 1000 °C for 6 and 14 days for ZnSe, CdSe and ZnS, respectively. The microscopic image of the Cr^{2+}:ZnSe powder prepared by annealing the ZnSe/CrSe mixtures at 1000 °C for 6 days is depicted in Fig. 1A. As one can see from Fig. 1A, this treatment resulted in the formation of microcrystalline powders of ~20 μm average grain size. Fig. 1B and C depict images of the Cr:ZnSe polymer film (0.18 mm thick) and liquid solution (12.5 mm × 40 mm × 1 mm quartz cell) of Cr-doped ZnSe and ZnS powder samples, respectively. The polymer and liquid samples were prepared in the following steps: (1) mixing the Cr:ZnS or Cr:ZnSe powders and commercially available polymer Teflon-AF 2400 at the 1:1 wt% ratio; (2) dissolving mixed samples (polymer Teflon and Cr-doped powders, 1:1 wt%) with the solvent (Fluorinert FC-77, Sigma) over a period of one day; (3) pouring the obtained liquid samples on a glass microscopic slide and subsequent solvent evaporation at RT for a period of 3 h. After solvent evaporation a good quality film of 0.18 mm thickness was peeled off the glass microscopic slide cut in a form of letter "A" of 7 mm height and 5 mm width.

3. Experimental setup

The mid-IR PL spectra, PL kinetics and lasing spectra (depicted in Fig. 2) were measured under direct $^5T_2 \leftrightarrow {}^5E$ excitation of the Cr^{2+} ions using 1700 nm radiation from the Spectra Physics Nd:YAG (355 nm) pumped optical parametric oscillator (OPO) operating with 5 ns pulse duration and repetition rate of 10 Hz. The PL or stimulated emission signal was then collected by a CaF_2 lens and detected using Acton Research Spectra-Pro 300i Spectrograph – liquid nitrogen cooled InSb detector (EGG Judson J10D-M204-R04 M-60) combination with a time resolution of 0.5 μs. The PL lifetime was measured by a Tektronix TDS 5104 Digital Phosphor Oscilloscope and the PL intensity signal was processed through a boxcar averager. All the measurements were performed at room temperature.

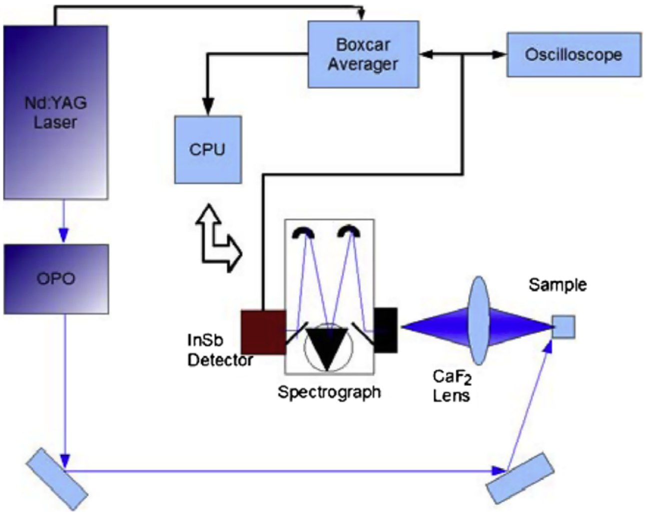

Fig. 2. Experimental setup for kinetic and luminescence measurements.

4. Measurements and results

The ^5D term of the ground state of free Cr^{2+} ($3d^4$) ions is split in a weak tetragonal T_d crystal field of the II–VI crystals into the ground $^5T_2$ and excited ^5E states. The spectral range of the $^5T_2 \leftrightarrow {}^5E$ spin-allowed transitions in Cr^{2+}-doped chalcogenides spans over 1.4–3.6 μm. RT lasing and PL spectra of Cr^{2+}:ZnSe powder, polymer film and polymer liquid solution are shown in Fig. 3A. Fig. 3A also demonstrates PL spectra of ~10 μm grain size Cr^{2+}:ZnSe powder annealed at 1000 °C for 6 days for different pump energies. As one can see in the Fig. 3A, at low pump energy the measured PL spectrum (curve 0.3 mJ, (i) is typical for the $^5T_2 \leftrightarrow {}^5E$ chromium transition in the bulk ZnSe host. Further increase of the pump energy above threshold (Fig. 3A, curves, 4 mJ (81.6 mJ/cm^2), (ii) polymer liquid solution; 5 mJ (102 mJ/cm^2), (iii) polymer film; and 6 mJ (122.4 mJ/cm^2), (iv) powder) results in appearance of intensive, much narrower stimulated emission, which central peak (2355 nm) is shifted to the longer wavelengths and practically corresponds to the peak of the Cr^{2+}:ZnSe gain spectrum. RT lasing spectra of Cr-doped ZnS, ZnSSe, ZnSe, and CdSe powders are depicted in Fig. 3B. Emission peaks of the Cr:ZnS (2241 nm), Cr:ZnSSe (2330 nm), Cr:ZnSe (2355 nm) and Cr:CdSe (2632 nm) powder samples correspond to the parity spin allowed electronic transitions between the excited ^5E and ground $^5T_2$ states.

Fig. 4A shows the dependence of the intensity of Cr^{2+}-doped ZnSe powder, polymer film, and polymer liquid solution emissions

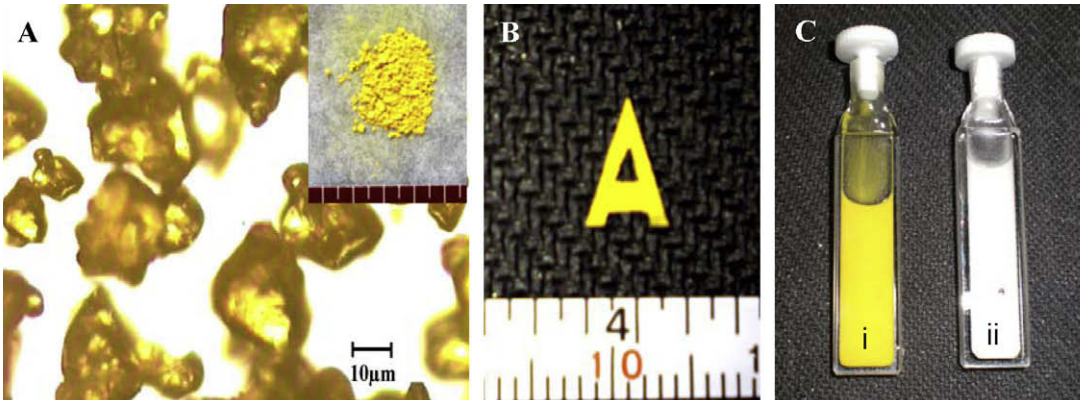

Fig. 1. Microscope images of the Cr^{2+}:ZnSe powders (A) with 20 μm average grain size, (B) polymer film (0.180 mm thick) based on mixture of Cr^{2+}:ZnSe powder and Teflon (1:1 wt%) and cut in a form of a letter "A", (C) liquid solution (12.5 mm × 40 mm × 1 mm quartz cell) of Cr^{2+}:ZnSe (i) and Cr^{2+}:ZnS (ii) powders and Teflon (1:1 wt%).

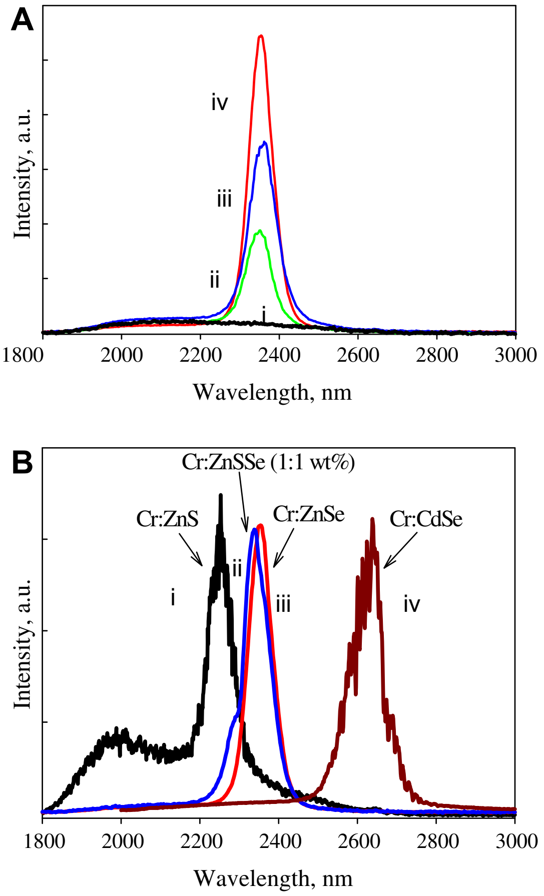

Fig. 3. (A) Room temperature emission spectra of Cr^{2+}:ZnSe in liquid (ii); polymer film (iii) and ~20 μm size powder (i, iv) for different pump energies (i, E_p = 0.3 mJ (6.12 mJ/cm^2); ii, E_p= 4 mJ (81.6 mJ/cm^2); iii, E_p= 5 mJ (102 mJ/cm^2); iv, E_p= 6 mJ (122.4 mJ/cm^2)); spectra (i) and (iv) demonstrate difference of the Cr:ZnSe powder emission spectra when pumped below (i) and above (iv) laser threshold. (B) Lasing spectra of the powder samples, (i) Cr:ZnS; (ii) mixed Cr:ZnSe; Cr:ZnS (1:1 wt%; Cr:ZnSSe); (iii) Cr:ZnSe; and (iv) Cr:CdSe measured at RT at 1700 nm excitation for pump spot diameter (ii, iii) 2.5 mm and (i, iv) 1.5 mm.

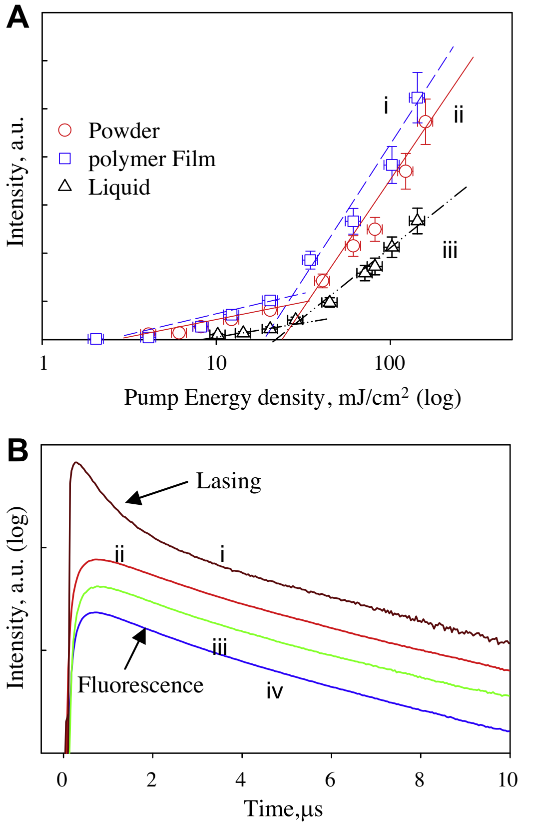

Fig. 4. Room temperature output emission intensity versus pump energy density for Cr^{2+}:ZnSe powder annealed at 1000 °C for 6 days (A) in (i) polymer film, (ii) powder, and (iii) liquid solution. (B) Cr^{2+}:ZnSe PL lifetime kinetics (logarithmic scale) for pump energy below (ii, powder; iii polymer film, and iv, liquid solution) and above (i, polymer film) laser threshold measured at RT at 1700 nm excitation for pump spot diameter 2.5 mm.

at 2355 nm versus the pump energy densities. The output–input characteristics clearly demonstrate the threshold-like behavior of the output signal with the threshold energy density of 0.4 mJ (8.1 mJ/cm^2) (i), 0.4 mJ (8.1 mJ/cm^2) (ii) and 1 mJ (20 mJ/cm^2) (iii) for powder, polymer film and polymer liquid solution, respectively. The threshold energy levels for Cr^{2+}:ZnS, Cr^{2+}:ZnSSe, and Cr^{2+}:CdSe powders are summarized in Table 1. Several reasons could be responsible for the big difference of the lasing thresholds for different powders. First of all it is the influence of the spot size on the threshold pump energy density value. The next factor relates to different chromium concentration. In addition, different powders feature different chromium diffusion coefficient resulting in different chromium distributions in the grains of the doped powders. Finally, different refractive indices cause different scattering lengths giving rise to different values of positive feedbacks for lasing process. Indeed, the comparison under the same excitation condition of mixed Cr:ZnSe/S and pure Cr:ZnSe powders random lasing shows that the mixture of low index of refraction ZnS to Cr:ZnSe powder results in the increase of laser threshold. The threshold pump energy density for Cr^{2+}:ZnSe film was as low as ~8.1 mJ/cm^2, which is similar to that of the powder sample. The PL kinetics of Cr^{2+}:ZnSe powder measured at 2355 nm at RT is shown in Fig. 4B. The RT luminescence lifetime of ZnSe powder annealed at 1000 °C for 6 days was 3.3 μs. Moreover, the PL lifetimes of polymer film and polymer liquid solution of kinetics were ~3.2 μs each, which is shorter than the 5 μs lifetime typical of Cr^{2+}-doped bulk crystal. We assume that Cr^{2+} excited state lifetime in ZnSe powder, polymer film, and polymer liquid solution were shorter than that in the bulk crystal due to additional channels of non-radiative relaxation.

Table 1
Summary of room temperature threshold pump energies and pump energy densities. (excitation wavelength 1700 nm, pump spot diameter was 2.5 mm for Cr^{2+}:ZnSe and mixed Cr^{2+}:ZnSe and Cr^{2+}:ZnS (1:1wt%; Cr^{2+}:ZnSSe); Cr^{2+}:ZnS and Cr^{2+}:CdSe pump spot diameter was 1.5 mm).

Samples	$n_{Cr}{}^{2+}$(cm^{-3})	Peak wavelength (nm)	Threshold pump energy (density), mJ, (mJ/cm^2)		
			Powder	Polymer film	Polymer liquid
Cr:ZnS	2.0×10^{19}	2241	3.5/(198)	3/(169)	5.5/(311)
Cr:ZnSSe	3.5×10^{19}	2330	1.1/(22.4)	1/(20)	3.5/(71)
Cr:ZnSe	5.0×10^{19}	2355	0.4/(8.1)	0.4/(8.1)	1/(20)
Cr:CdSe	1.0×10^{20}	2632	1.3/(73)		

5. Conclusions

In conclusion, for the first time to our knowledge we observed random lasing in Cr^{2+}:ZnS and Cr^{2+}:ZnSe polymer liquid solutions and polymer films. The threshold pump energy density of liquid solutions and polymer films were ~311 mJ/cm^2, ~169 mJ/cm^2, and ~20 mJ/cm^2, ~8.1 mJ/cm^2 for Cr^{2+}:ZnS and Cr^{2+}:ZnSe, respectively. In addition, we demonstrated a simple method of Cr^{2+}-doped ZnS, ZnSSe, ZnSe, and CdSe powder fabrication and realized RT mid-IR random lasing under optical intra-shell excitation of chromium. Threshold dependence of the powder emission, significant line narrowing, and lifetime shortening are clear evidence of Cr^{2+}-doped ZnS, ZnSSe, ZnSe, and CdSe powders lasing. Cr^{2+}:ZnS, Cr^{2+}:ZnSe, and Cr^{2+}:CdSe random powder lasing was achieved with the threshold pump energy density of ~198 mJ/cm^2, 8.1 mJ/cm^2, and 73 mJ/cm^2, respectively. Mixture of the different semiconductor hosts allows tuning oscillation wavelength from 2240 to 2630 nm. This technology provides a cost effective route for fabrication of mid-IR gain powder materials that is promising for scientific, technological, and defense-related applications.

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