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2.18 μm random laser action based on Cr^{2+}:ZnSe nanocrystalline particles

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ABSTRACT

An approach for fabricating Cr^{2+}:ZnSe nanocrystalline particles by 355 nm nanosceond laser ablation of polycrystalline micron-sized powder in liquid environment is presented. The scanning electron micrscope and X-ray diffraction results reveal that the products are ZnSe cubic sphalerite structured nanocrystalline particles with an average size of 50 nm. Based on the Cr^{2+}:ZnSe nanoparticles, typical random laser emissions centering at 2180 nm with a threshold of 0.35 mJ/pulse are observed for the first time. Compared to the micron-sized powder, it shows a blue-shift of 170 nm. With the pump energy increasing (above the threshold value), the decay time reduces to 30 ns from 1.2 μs. Our experimental results demonstrate that the Cr^{2+}:ZnSe nanoparticles random lasing emission appears in a wide pump wavelength range from 1500 to 1900 nm. The comparsions of the fluorescence, excitation spectra and threshold features between micron-sized particles and nanoparticles are also presented.

1. Introduction

Random laser (RL) is a class of optical structure in which light is multiply scattered owing to randomness and amplified by stimulated emission [1]. This new type of laser was first theoretically introduced by Ambartsumyan [2]. Great effort was made to achieve experimental demonstrations by Markushev et al. based on a Nd^{3+} doped ($Na_5La_{1-x}Nd_x(MoO_4)_4$) powder [3]. Random laser has been extensively investigated with a variety of materials and structures, such as liquid laser dye with scatterers [4–7], semiconductor powders [8–10], fibers [11,12], polymeric films [13,14], and dye-infiltrated opals [15,16]. Due to its low cost of fabrication, mirror-less cavity, and small size, the random lasers are attractive for many important applications, such as light-emitting devices [17] and medicine [18,19].

Nanocrystalline powder is a typical random laser system which has been explored extensively [20], but most of them are emitted in the wavelength range from visible to near-infrared. Middle-infrared (mid-IR) laser sources are in a great demand for a variety of scientific and technological applications, including non-invasive medical diagnostics, environmental monitoring, and military defense fields [21]. The results of recent researches indicated that transition-metal (TM) doped chalcogenides represents a category of solid state gain media with ultra-broad absorption and emission band in the mid-IR wavelength range [21–24]. In the same way, the nanocrystalline powders based on such gain media are promising mid-IR RL source. RL action based on Cr^{2+}:ZnS nanocrystal [22], Cr^{2+}:ZnSe micron-sized powders [23] and polymer film [24] have been successfully demonstrated. Several approaches have been developed to fabricate TM doped chalcogenides nanocrystal particles, for instance, laser ablation [21,22] and micro-emulsion method [25].

In this work, Cr^{2+}:ZnSe nanoparticles were fabricated by 355 nm (7 ns pulse duration) laser ablation (355 nm-NLA) of polycrystalline Cr^{2+}:ZnSe micron-sized powder in liquid environment. The scanning electron micrscope (SEM) and X-ray diffraction (XRD) results reveal that the products are ZnSe cubic sphalerite structured nanoparticles with an average size of 50 nm. Based on the Cr^{2+}:ZnSe nanoparticles, typical random laser emissions centering at 2180 nm with a threshold of 0.35 mJ/pulse are observed for the first time. Compared to the random laser spectra of micron-sized particles (centering at 2350 nm), the peak position of nanopaticles (around 2180 nm) shows a comparatively dramatic blue-shift (nearly 170 nm). The full width at half maximum (FWHM) of RL peak is about 45 nm. The decay time drops to 30 ns from 1.2 μs as the pump energies increase above the threshold, which is a proof for random laser emission of Cr^{2+}:ZnSe nanoparticles. Our experimental results demonstrate that the Cr^{2+}:ZnSe nanoparticles random lasing emission appears in a wide pump wavelength range from 1500 to 1900 nm. In order to demonstrate the unique laser charateristics for Cr^{2+}:ZnSe nanoparticles, the comparsions for the fluorescence and excitation spectra and threshold features between micron-sized particles and nanoparticles are

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presented. The excitation spectra peak positions of Cr^{2+}:ZnSe particles are varied with the sizes of particles. The threshold increases with a decreasing of particle size.

2. Experiments

2.1. Sample preparation

Cr^{2+}:ZnSe nanoparticles were prepared by laser ablation of polycrystalline Cr^{2+}:ZnSe powder in liquid environment. Initially, polycrystalline Cr^{2+}:ZnSe bulk was prepared by vapor phase thermal diffusion method. ZnSe crystal and the dopant chromium (Cr) powder were placed in the different parts of ampoules which would be vacuum-sealed (10^{-3} Pa). Following, the thermal diffusion was carried out at the temperature of 1000 °C for 12 days. The concentration of the dopant Cr^{2+} is about 5×10^{19} cm^{-3}. In order to increase the efficiency of laser ablation, the Cr^{2+}:ZnSe bulk was mechanically grinded to micron-sized powders (the average size ~3 μm) as targets to be laser ablated. The investigated Cr^{2+}:ZnSe nanoparticles were fabricated by the radiation of a 355 nm third harmonic generation (THG) of Nd^{3+}:YAG nanosecond laser system (INNOLAS), and Table 1 gives the detail parameters of the laser ablation system.

In the ablation experiment, ~2 g Cr^{2+}:ZnSe micron-sized powder were dispersed in deionized water inside a quadrate quartz cuvette ($2\times2\times8$ cm^3). The laser beam was focused into the water-suspended Cr^{2+}:ZnSe micron-sized powder by a lens ($f=7$ cm), meanwhile the dispersed fluid was stirred with a constant rotate rate (1000 round/min) by a magnetic stirring apparatus. In order to ablate sufficiently, the ablation process was sustained for 15.5 h. After the ablation process, the samples were ultrasonically dispersed and centrifuged to separate the remaining micron size particles. Finally, the samples were dried at 100 °C.

Table 1
The detail parameters of the 355 nm laser ablation system.

Laser system	THG of Nd^{3+}:YAG
Center wavelength	355 nm
Pulse duration	7 ns
Repetition rate	10 Hz
Energy	10 mJ/pulse
Spot area	0.1 mm^2

Fig. 1 illustrates the SEM morphologies of the Cr^{2+}:ZnSe micron-sized particles (Fig. 1(a)) and 355 nm-NLA nanoparticles (Fig. 1(b)). Obviously, it can be seen from that the micron-sized particles (Fig. 1(a)) are irregularly shaped with 3 μm average size. The results can be confirmed by the particle size distribution histogram (left inset of Fig. 1(a)). Fig. 1(b) shows the SEM results of Cr^{2+}:ZnSe nanoparticles produced by 355 nm-NLA, the nanoparticles are sphere shaped with an average size of ~50 nm. Similar observations have been obtained in the reports of [26,27]. It is remarkable to notice that the colors of the two samples' water dispersion are different, yellow for micron-sized powder and red for the 50 nm nanoparticles. The quantum-size effect of nanoparticles could explain the observation. As the size decreases, the absorption for the short wavelength in visible wavelength rang gets stronger, resulting that the color changes to red from yellow.

Fig. 2 gives the XRD patterns of the two kinds Cr^{2+}:ZnSe particles and ZnSe bulk. The XRD researches were performed by (θ–2θ) angle X-diffraction (X'Pert Pro MPD, Philips Research) with Cu Kα anode. The XRD peaks of the powders can be indexed as the

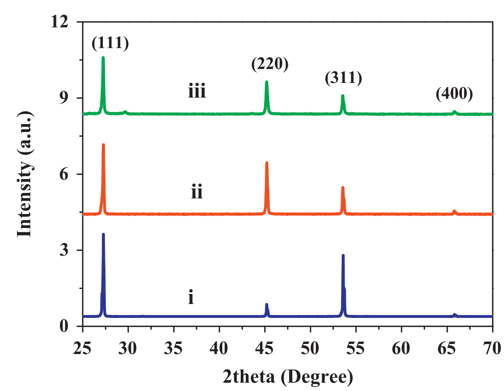

Fig. 2. The XRD patterns of ZnSe bulk (i), micron-sized particles (ii) and 50 nm (355 nm-NLA) nanoparticles (iii).

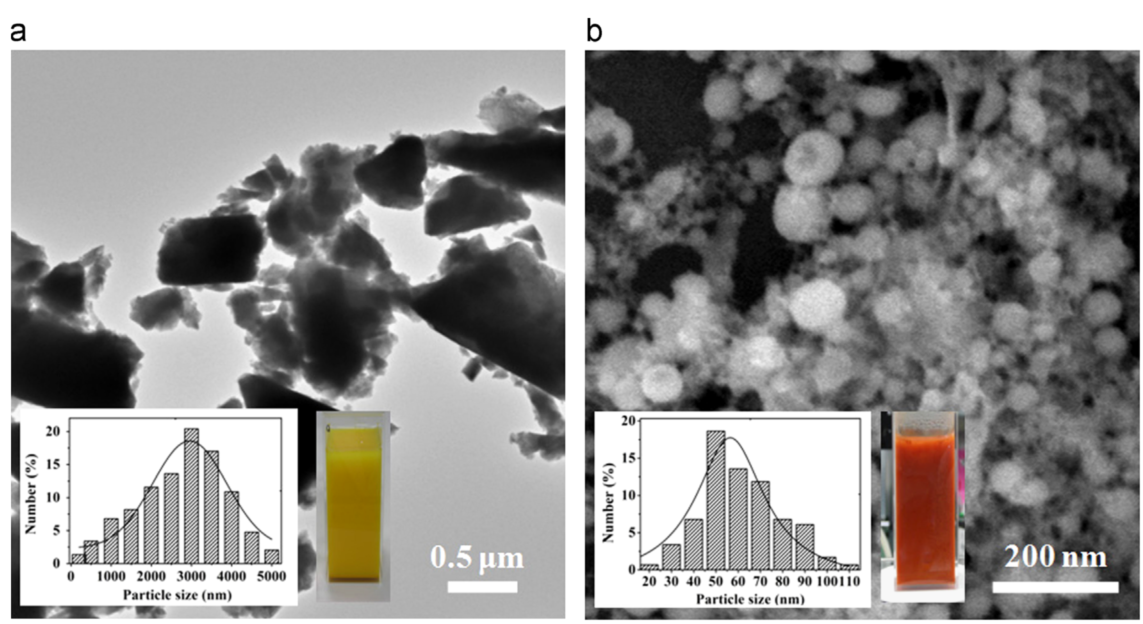

Fig. 1. The SEM images of micron-sized particles (a), and 355 nm-NLA nanoparticles (b). The left insets in the figures are particle size distribution histograms, the solid line is the log-normal fit from which the average particle size is calculated. The right insets are photographs of the two samples' water dispersion.