Crystalline Cr^{2+}:ZnSe/chalcogenide glass composites as active mid-IR materials

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We propose new transition metal (TM)-doped ZnSe/As_2S_3:As_2Se_3 composite materials for mid-IR fiber lasers. The composites are the suspension of crystalline micro- and nanosized TM^{2+}:ZnSe or TM^{2+}:ZnS powders in chalcogenide glasses with the refraction index matching. Mid-IR room-temperature lasing of Cr^{2+}:ZnSe/As_2S_3:As_2Se_3 microcomposite material is demonstrated at the 2.4 μm wavelength. © 2011 Optical Society of America

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Recent progress in solid-state lasers based on single and polycrystalline chromium-doped II–VI semiconductor materials (ZnS, ZnSe, CdSe) makes them the laser sources of choice when one needs a compact system with tunability over the 1.9–3.6 μm spectral region [1]. Output powers exceeding 10 W and efficiency up to 70% have been demonstrated using Cr^{2+}-doped ZnS and ZnSe. A further increase of output power requires thorough thermal management in the active element. Among different approaches to control beam quality and thermal lensing, a waveguide and fiber lasers are very promising for a variety of applications.

In spite of years of research, all the attempts to fabricate Cr:II–VI media in fiber geometry have not been successful. On the contrary, the technology of mid-IR passive fibers based on chalcogenide glasses has come of age [2], and they are readily available from different vendors. Chalcogenide glasses are of interest for mid-IR fiber-laser applications [3] due to their wide IR transparency range, capability to vary the refractive index, and photostructural effects under exposure to radiation in the bandgap region [4]. Recently, refractive index values ranging from $n = 2.1$ to 2.4 have been reported for As_2S_3 chalcogenide glasses, enabling a pathway to refractive index optimization and matching ZnS ($n = 2.2$) and ZnSe ($n = 2.4$) crystals [5]. Divalent Cr^{2+} and Fe^{2+} ions require tetrahedral crystal-field coordination to produce energy level structures suitable for effective tunable mid-IR lasing [1,6]. Chemically stable divalent states of chromium and iron as well as their tetrahedral crystal-field coordination are natural for II–VI crystal hosts (ZnS, ZnSe, CdSe), but they are not possible in the chalcogenide glass media. Capitalizing on the features of ZnS/ZnSe crystals to produce tetrahedral coordination of mid-IR laser active Cr^{2+} and Fe^{2+} ions and chalcogenide glass hosts enabling fiber geometry and matching of the refractive index to II–VI crystals, we propose a new nano- and microcrystalline Cr^{2+}:ZnSe/chalcogenide glass composite media. In this Letter, we report the fabrication of laser active Cr^{2+}:ZnSe/As_2S_3:As_2Se_3 composite material and the first (to our knowledge) demonstration of their mid-IR lasing. These composite materials are very promising for mid-IR fiber-laser applications.

One of the crucial steps in fabrication of composite mid-IR gain media is related to preparation and characterization of transition metal (TM)-doped II–VI powders with different grain sizes. The majority of methods of fabrication of II–VI semiconductor nanosize powders are based on chemical approaches in which a variety of functional groups are used to stabilize nanoparticles and serve as capping agents. Even a small amount of residual organic molecules used in powder synthesis may reabsorb or quench mid-IR luminescence. That is why we used an entirely physical approach to fabrication of doped nanopowders using laser ablation of bulk TM-doped targets. Overall, we prepared several types of the Cr^{2+}-doped ZnS and ZnSe powders for development of the composite media: (i) nanopowders prepared by laser ablation of Cr^{2+}-doped ZnSe and ZnS crystals, (ii) microsize powders prepared by annealing of commercial ZnSe and CrSe powders followed by mechanical grinding, and (iii) microsized powders prepared by mechanical grinding of Cr^{2+}:ZnSe or Cr^{2+}:ZnS crystals.

Nanopowders were prepared by laser ablation of bulk polycrystalline TM^{2+}-doped II–IV (i.e., ZnS, ZnSe) semiconductor targets in liquid and gaseous environments using the radiation of an Nd:YAG laser (1064 nm) with a 30 ps or 5 ns pulse duration. Initially, TM^{2+}-doped ZnS and ZnSe polycrystalline targets were prepared by the thermal-diffusion method described elsewhere [7–10]. The average TM^{2+} ion concentration was 10^{18}–10^{19} atoms/cm^{-3}. The variation of laser wavelength, pulse duration, ablation environment, and additional UV treatment produced nanocrystals with different (3, 11, 27, and 250 nm) sizes [11,12]. The average size of the nanocrystals was found using Scherrer's equation and the width of the x-ray diffraction peaks. These findings were also confirmed by TEM studies. Figure 1(a) shows a TEM image of 27 nm Cr^{2+}:ZnS nanoparticles prepared in an Ar atmosphere using a 30 ps Nd:YAG laser. Room-temperature photoluminescence (PL) spectra of Cr^{2+}, Co^{2+} and Fe^{2+}-doped ZnS and ZnSe nanocrystals prepared by laser ablation are demonstrated in Fig. 1(b). As can be seen, TM^{2+}-doped nanocrystals feature a broad PL spectra over a 1.8–5.5 μm spectral range. These luminescence bands

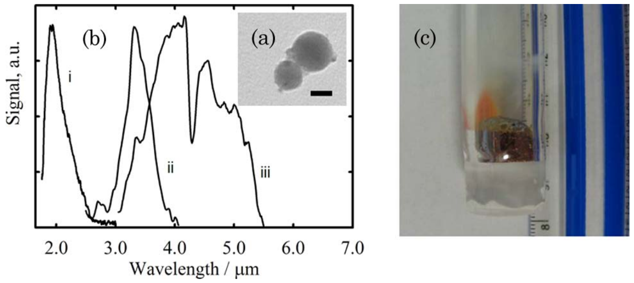

Fig. 1. (Color online) (a) TEM image corresponding to 27 nm Cr^{2+}:ZnS nanoparticles (scale bar shown in the figure equals 20 nm). (b) PL of TM-doped II–VI nanoparticles prepared by laser ablation in water: (i) Cr^{2+}-doped ZnS, (ii) Co^{2+}-doped ZnSe, and (iii) Fe^{2+}-doped ZnSe. (c) Glassy Cr^{2+}:ZnSe/As_2S_3:As_2Se_3 composite materials heat treated at 290 °C.

are typical for intrashell transitions of TM^{2+} ions in the tetrahedral coordination.

Microsized Cr^{2+}:ZnSe powders were produced by mechanical grinding of Cr^{2+}-doped polycrystalline ZnSe and ZnSe samples or by thermal annealing of the commercially available ZnSe and ZnS powders mixed with the appropriate amount of CrSe and CrS impurities. Initially, pure ZnSe(ZnS) and CrSe(CrS) powders with an average grain size of ~5–10 μm were uniformly mixed by a mechanical shaker. At the second stage, the obtained material was sealed into an evacuated (10^{-4} Torr) quartz ampoule and annealed at 1000 °C for three days. This treatment resulted in formation of chromium-doped microcrystalline powders with an ~10–20 μm average grain size. A subsequent mechanical grinding of these powders reduced the average grain size to ~1 μm [13]. The advantage of this method is that the crystal growth stage is completely eliminated.

The Cr^{2+}:ZnSe/As_2S_3:As_2Se_3 composites were prepared by using two different methods. The first type was prepared by heat treatment of the appropriate compounds under vacuum. The mechanical mixtures of 1 g of amorphous As_2S_3 [Amorphous Materials, Inc., purity ≥1 part in 10^6 (ppm)], 50 mg of amorphous As_2Se_3 (Amorphous Materials, Inc., purity ≥1 ppm) and 0.5 g of Cr^{2+}:ZnSe were ground using an agate pestle and mortar into fine powders. The powders were sealed in evacuated quartz ampoules and heat treated at different temperatures 290 °C–600 °C [see Fig. 1(c)]. The second type of sample was prepared by casting and was prepared by drying Cr^{2+}:ZnSe powder suspension in As_2S_3:As_2Se_3 propylamine (Sigma Aldrich, purity ≥99%) solution. The solution was prepared by dissolving 1.0 g of As_2S_3 and 50 mg of As_2Se_3 in polyamine under an Ar atmosphere. The Cr^{2+}:ZnSe fine powder in the amount of 0.5 g was added to the solution. The solution was cast onto a sapphire wafer and a ZnS optical window in the appropriate amount to obtain 100 μm thick films. Films were dried under an Ar atmosphere for 24 h and heat treated under vacuum at 180 °C for 2 h.

The mid-IR PL spectra, PL kinetics, and lasing spectra were measured under 1560 nm D_2-Raman shifted Nd:YAG laser excitation with a pulse duration of 5 ns. The PL lifetime was measured by a liquid-nitrogen-cooled InSb detector with a 0.5 μs response time. All measurements were performed at room temperature. The samples demonstrated a mid-IR PL typical for Cr^{2+} ions in the tetrahedral coordination in the ZnSe host between 1.8 and 3.0 μm [see Fig. 2(a), curves i and iii] with a PL kinetic lifetime of ~5 μs [see Fig. 2(b), curves i and ii].

The mid-IR high optical gain and low passive absorption of Cr^{2+}:ZnSe/As_2S_3:As_2Se_3 composite materials were demonstrated via random lasing experiments, when a positive laser feedback sufficient for laser oscillation is raised from scattering in the active media. Observed in Fig. 2, the threshold dependence of the emission intensity, significant line narrowing in spectral domain, and lifetime shortening are clear evidence of random lasing in the fabricated composite. Figure 2(a) (curve iii) shows stimulated emission spectra of the Cr^{2+}:ZnSe/As_2S_3/As_2Se_3 composite material heat treated at 290 °C at pump energies above the lasing threshold. The maximum signal was at 2350 nm, which corresponds to the maximum of the gain spectra of Cr^{2+}:ZnSe and is the typical lasing wavelength of Cr^{2+}:ZnSe in the regime of random oscillations. Stimulated emission was accompanied by a considerable shortening of the kinetics of the signal, as shown in Fig. 2(c) (curve iii), as well as by a threshold-like behavior of the output signal. The inset in Fig. 2(b) shows the dependence of the averaged intensity of emission at 2350 nm versus pump energy. The output/input characteristics clearly demonstrate a threshold-like behavior of the output signal with the threshold energy level of 13 mJ.

We believe that the passive losses due to the residual solvent absorption in the second type of samples, e.g., As_2S_3/As_2Se_3 sample dissolved in propylamine, prevented stimulated emission.

In summary, the proposed TM-doped ZnS:ZnSe/As_2S_3:As_2Se_3 composite materials with index matching of II–VI and V–VI components represent a new way for the design of mid-IR laser active fibers. We report the first (to our knowledge) room-temperature laser oscillation of a Cr^{2+}:ZnSe/As_2S_3:As_2Se_3 compound at 2.4 μm.

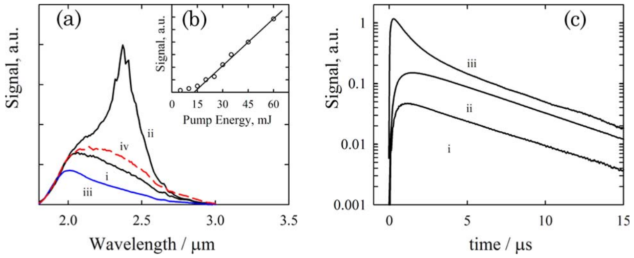

Fig. 2. (Color online) (a) PL spectra, PL kinetics, and lasing spectrum of Cr^{2+}:ZnSe/As_2S_3:As_2Se_3 composite materials: (i) PL spectrum of As_2S_3/As_2Se_3 (100/5 weight ratio) mixed with 50% (weight ratio) of Cr^{2+}:ZnSe micropowder sealed in an evacuated quartz ampoule and heat treated at 290 °C for 24 h, (ii) lasing of the same compound as shown in (i), (iii) PL spectrum of As_2S_3/As_2Se_3 (100/5 weight ratio) dissolved in propylamine mixed with 50% (weight ratio) of Cr^{2+}:ZnSe micropowder, and (iv) PL spectrum of Cr^{2+}:ZnSe bulk sample given for comparison. (b) Output signal versus input pump energy of sample (i). (c) PL kinetics of (i) sample prepared from propylamine solution (same as above) and (ii) sample heat treated at 290 °C (same as above); curve (iii) shows kinetic shortening due to random lasing of the Cr^{2+}:ZnSe/As_2S_3:As_2Se_3 composite.

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