Hot-pressed ceramic Cr^{2+}:ZnSe gain-switched laser

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Abstract: The technology of hot-pressed Cr^{2+}:ZnSe ceramic preparation is reported. Comparative gain-switched lasing of hot–pressed ceramic and CVD grown Cr^{2+}:ZnSe samples with slope efficiencies up to 10 % and output energies up to 2 mJ were demonstrated. This is a milestone in the development of future large scale mid-IR laser systems based on ceramic TM^{2+}:II-VI materials. This evolving technology has excellent potential as media for practical low cost, high power mid-IR laser applications.

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OCIS codes: (160.3380) Laser materials, (140.3580) Lasers, solid-state

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1. Introduction

There is a growing demand for affordable, compact, room temperature and broadly tunable mid-infrared (mid-IR) laser sources. In 1996 and 1997 L. D. DeLoach et. al.[1] and R. H. Page et al.[2] performed detailed spectroscopic studies of several II-VI chalcogenide hosts with different divalent transitional metal ions (TM^{2+}) dopants as potential mid-IR laser materials. These materials have many advantages including near unity fluorescence quantum efficiency at room temperature, high heat conductivity ($0.18W \ cm^{-1} \ K^{-1}$), high gain cross section, and no excited state absorption. Since then, Cr:ZnS [3,4], and Cr:ZnSe [5-9] laser demonstrations over the 2-3 μm spectral region in CW, free-running long pulse, Q-switched and mode-locked regimes of operation have been reported in many cases for both single crystal and polycrystalline hosts. These sources have a variety of applications, such as eye-safe medical laser sources, eye-safe laser radar (LIDAR), remote sensing of atmospheric constituents, optical communication, and numerous military applications such as target designation, obstacle avoidance and infrared counter measures.

Currently the state of the art in TM:II-VI laser systems rely either on single crystal, or vapor grown polycrystalline materials. Both of these materials have particular drawbacks in terms of crystal doping. The commonly used doping methods are in melt [10], vapor growth [11,12], or after growth thermo-diffusion doping [3,4,12]. For example, bulk Cr^{2+}:ZnSe crystals can be obtained by including the dopant in the initial charge in the melt [10] or through vapor growing techniques [10]. Under atmospheric pressure ZnSe sublimation occurs at a temperature above ~400 °C which is lower than that of the melting point [13]. Therefore to use melt growth techniques, in addition to high temperature (1515 °C), it is necessary to apply high pressure (75 x10^2 KPa) [13]. High temperature melt growth is often accompanied by uncontrolled contamination. This contamination can lead to undesirable and parasitic absorptions. Control of the amount of Cr^{2+} ions incorporated in the crystal is difficult when using vapor growth techniques [11,12]. Doping of host crystals/polycrystals that are already grown allow for another method of TM incorporation, thermal diffusion. This technique utilizes thermally activated diffusion of transition metal ions into the II-VI crystals [3,4,12]. However this technique has several drawbacks as well. These drawbacks include poor uniformity doping, large concentration gradients, and the procedure has poor repeatability. These problems with the control of dopant concentration are not appropriate for the fabrication of low cost, large-scale samples for high-energy mid-IR applications. Thus another method of crystal growth is required that will allow for large-scale crystal production in a timely and efficient manner.

In the 1960's researchers hypothesized that a dense polycrystal of a pure material will be optically indistinguishable from a single crystal of the same composition. In 1966 Hot-Pressed CaF_2 doped with dysprosium was reported as the first successful ceramic laser material [12]. Since then many advances have been made in Nd:YAG ceramics. Thirty years

later advances in ceramic productions have led to the Konoshima chemical Co. Ltd. NTVS (nano crystalline technology and the vacuum sintering) method [14,15]. This method shows laser action equivalent and in some cases surpassing that of Nd:YAG single crystals. Thus ceramic laser materials show a promising future not only for their optical properties but also for thermal and economic properties [16-19].

The laser levels associated with Cr^{2+} in ZnSe are $^5T_2$ the ground state and ^5E the first excited state for chromium. These levels have the same spin which implies that they will have a large cross-section for emission. Higher lying levels have a lower spin thus reducing the probability for excited state absorption. The $^5E \rightarrow {}^5T_2$ transition is accompanied by a photon emission with energy within the middle infrared region of the spectrum (2-3 µm). It is for these reasons that such a system is of interest.

The objective of this study is to demonstrate that hot-pressed ceramics are a promising and viable "alternative route" for the synthesis of large-scale mid-IR laser media based on chromium doped ZnSe. Hot-pressed Cr:ZnSe laser materials can be made quickly, with nearly any dopant concentration, and many varied geometries. Such hot-pressed ceramics are the initial step in a research path that looks to be as promising as that of early research into Nd:YAG ceramics.

2. Sample preparation

Hot-Pressed ceramic crystal preparation is a multi-step process involving powder preparation and a multi-step heating and pressing procedure. The powder preparation for hot-pressing was performed by mixing pure ZnSe and a preliminary prepared mixture of ZnSe-CrSe (1 mol %). This mixture was subjected to grinding in a "Fritch" spherical agate mortar. This ground mixture contains particles with diameters less than 10 µm. Prior to hot pressing, the samples were first briquetted at room temperature under a pressure of 60 MPa. Pyrolitically densed graphite "MPG" was used for preparation of the press-form and punch. The internal diameter of the press-form was ~15mm. The mass of the powder used to prepare a pellet was chosen such that the final height of the pellet is 20-25 mm. These sample pellets, contained 0.01, 0.03, 0.05, and 0.1 mol % of CrSe. Each sample was then further hot-pressed. Initial heating to 900K was performed in a resistive heating furnace. Further heating was achieved by applying an electric current through the sample. This current heated the samples to 1400-1500 K. In conjunction with the heating, the samples were subjected to axial compression with a pressure of 30-35 MPa. After 10-15 minutes of this hot-pressing samples were cooled to room temperature. Then final cutting and polishing was performed. The final samples had a diameter of 15 mm and a height of 10.5 mm.

Hot-pressed fabricated samples were compared with the polycrystalline samples prepared from a 1 mm thick ZnSe optical window, which was doped using thermal diffusion. The polycrystalline samples of ZnSe were grown by chemical vapor deposition. Doping of the 1 mm thick ZnSe polycrystalline substrates were performed by after growth thermal diffusion of Cr. Doping of ZnSe samples was achieved by inserting ZnSe crystals together with CrSe powder into quartz ampoules that were evacuated and then sealed, under 10^{-4} Torr pressure. Thermal diffusion was performed at 1000°C for 14 days and a Cr:ZnSe polycrystal with absorption coefficient of ~10 cm^{-1} was produced.

3. Experimental results

Hot-pressed ceramic Cr:ZnSe was characterized in several regimes to compare it to conventionally thermally diffused Cr:ZnSe polycrystalline samples. Such techniques as X-Ray Diffraction (XRD), mass density measurements, absorption and emission spectrum comparisons were made between the two classes of materials. The following sections discuss the findings and then present the laser action that was achieved in this hot-pressed ceramic material.

3.1 X-Ray diffraction

The ceramic and CVD grown samples were investigated using x-ray diffraction (XRD) to determine the crystalline grain size range. This XRD inspection was performed using (θ-2θ) angle x-ray diffraction (Philips X-Pert MPD, The Netherlands) with a Cu K-alpha anode. Spectra were taken from 23° to 80° (2θ) at a step size of 0.05 degrees. As seen in fig. 1 the
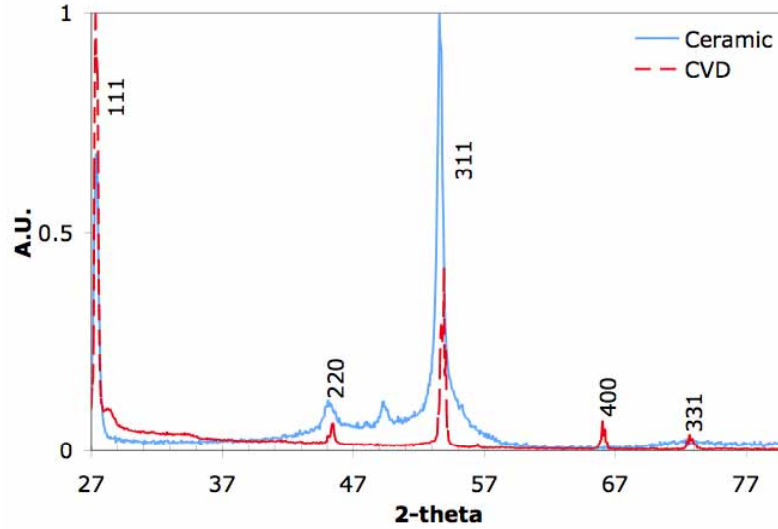

Fig. 1. XRD spectrum of CVD grown and Ceramic Cr:ZnSe samples.

location of the strongest XRD spectra peaks (111, 220, and 311) for the ceramic samples were in agreement with that of the polycrystalline CVD grown samples, thus confirming that the ceramic samples are indeed polycrystalline ZnSe in the cubic crystal isomer. The ceramic crystal grains were slightly oriented as seen by the lack of the 400 peak and week 331 peak. The Scherrer equation was used to determine the grain size range.

$$t = \frac{\lambda}{B\cos(\theta)} \tag{1}$$

$$B = \sqrt{B_m^2 - B_s^2} \tag{2}$$

Where B_m is the measured full width at half max (FWHM) of the XRD peak, B_s is the peak spread due to the x-ray detector and λ is the wavelength of the incident x-rays. B_s was calculated using a linear fit to the width of peaks over large distributions of angles using a large grain carbon sample. Peak fitting was performed on the 111 and 311 peaks. Reasonable fits were achieved using the superposition of two lorentizan curves for each peak (see Fig. 2). The numerical fitting was performed using nonlinear ψ^2 fitting in Mathematica®.

$$L(\theta) = \frac{1}{\pi} \frac{\frac{1}{2}\Gamma}{(\theta - \theta_o)^2 + \left(\frac{1}{2}\Gamma\right)^2}, \Gamma = FWHM \qquad (3)$$

One of these lorentzian peaks had a large FWHM and the other a small FWHM corresponding to distributions with small and large grain sizes respectively. The Scherrer equation was applied to both widths determined from the peak fitting to determine the average grain size for each distribution. This yields an estimate of the average grain size to be on the order of ~30-40 nm. The estimated width that corresponds to a large FWHM suggests that the larger grains are suspended or at least mixed in a matrix of amorphous particles that have little to no long range (>10 nm) order. We suggest that these two sets of grain sizes stem from the anisotropy of applied stress during sample manufacture.
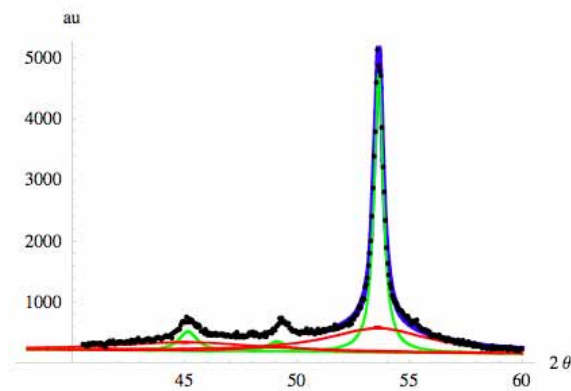
Fig. 2. The XRD spectrum (black dots) is fit with the superposition of two lorentzian curves (red, green) so that a reasonable fit (blue) is made to the data for the 311 peak.

3.2 Mass density

Mass density measurements were made of both the ceramic and polycrystalline samples. This measurement was made to ensure that there are no trapped air bubbles or other small, optically transparent defects within the ceramic matrix. This comparison showed a density of 5.1 ± 0.1 g/cm^3 for the polycrystalline sample and 5.15 ± 0.05 g/cm^3 for the hot-pressed ceramic samples. These values show reasonable agreement further confirming that hot-pressed ceramic samples can be of useable quality as polycrystalline samples.
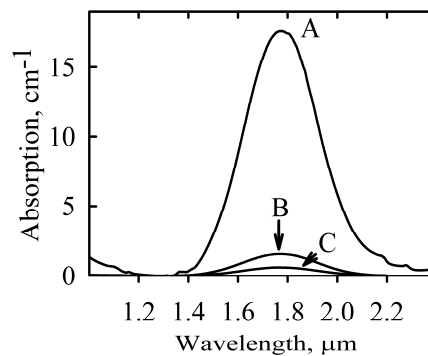

Fig. 3. Absorption spectra of Cr^{2+}:ZnSe samples. (A) polycrystalline, thermo-diffusion doped Cr^{2+}:ZnSe; (B) and (C) hot-pressed Cr^{2+}:ZnSe ceramics

3.3 Optical characterization

The absorption spectra for all of the samples were measured using a "Shimadzu UV-VIS-NIR-3101PC" spectrophotometer. The absorption spectra of the samples are shown in Fig. 3. Both polycrystalline, after growth doped, and Hot-Pressed ceramic samples feature a broad absorption band centered at 1.78 μm. This absorption peak indicates that chromium is indeed in the optically active 2+ state, for all the samples studied including the hot-pressed ceramic material.
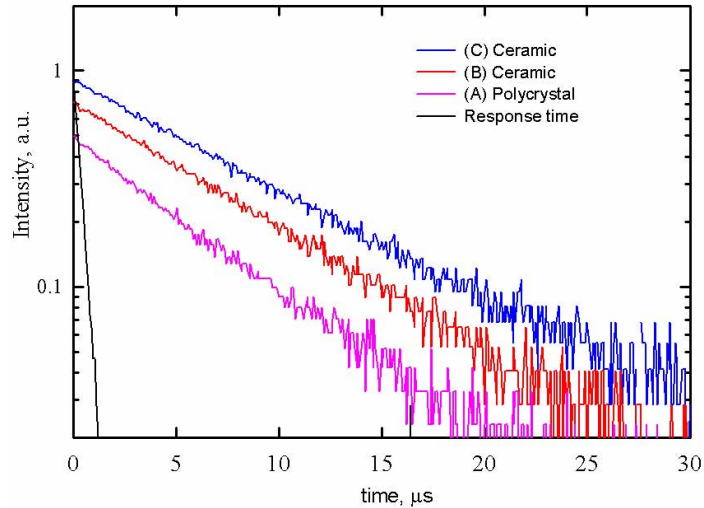

Fig. 4. Luminescence lifetime measurements for hot-pressed Ceramic and polycrystalline samples under 1.91 µm pumping.

Luminescence lifetime measurements were made on the ceramic crystals using a pump source of 1.91 µm. This pumping was from the 1st stokes line of the hydrogen Raman shifted fundamental of a Nd:YAG Q-switched laser. These measurements show that the luminescence lifetime corresponding to the ceramic samples is in good agreement with that of the lifetime of conventionally thermally defused polycrystalline samples (Fig. 4) and indeed the active centers in the ceramic samples have the same optical properties as that in previously studied polycrystalline samples.

3.4 Laser action

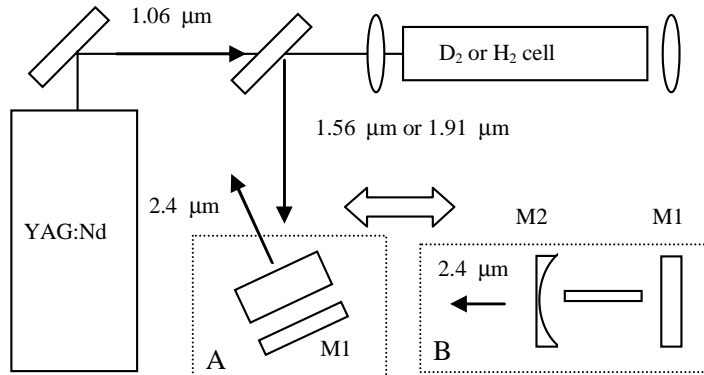The laser cavity for the ceramic samples consisted of a single flat high reflectivity mirror

Fig. 5. Schematic diagram of gain-switched hot-pressed ceramic (A) and polycrystalline (B) Cr^{2+}:ZnSe lasers.

(99.5%) placed less than 1 mm from the sample and Fresnel reflection (R= ~18%) from the front face of the ceramic sample as an output coupler. The ceramic crystals were pumped at the Brewster angle (~67.4°) from the front surface with a pump spot diameter of 6.5 mm [see Fig 5(A)]. The laser set-up for the polycrystalline samples consisted of a 99.5% reflecting flat mirror (M1) and an output coupler with radius of curvature of 20 cm and reflectivity 80% (M2) [see Fig 5(B)]. The cavity was 2.5 cm long with the polycrystalline sample ~2 mm from the flat mirror (M1). The crystal was side pumped normal to the direction of laser output with a spot diameter of 3.9 mm. All pumping was achieved using the 1st stokes line of the Raman shifted fundamental of a Nd:YAG Q-switched laser, shifted in a hydrogen Raman cell. This Raman shifted line is of wavelength 1.91µm (see Fig. 5).

The input-output characteristics of the lasers are shown in Fig. 6. The relative slope

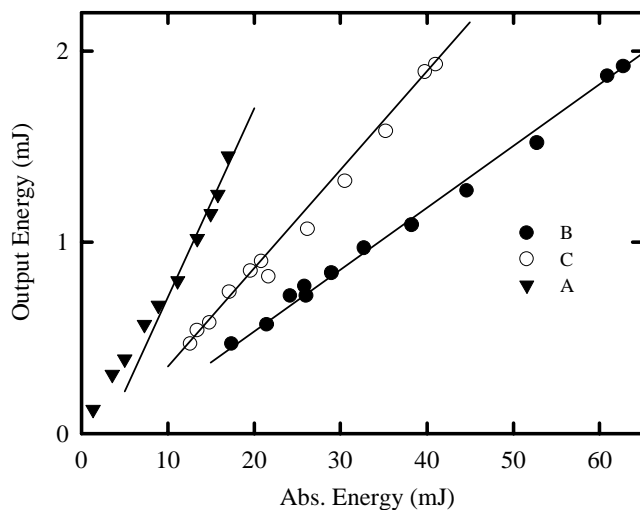Fig. 6. The output characteristics of the gain-switched Cr^{2+}:ZnSe based on polycrystalline sample (A) and hot-pressed ceramic (B and C).

efficiencies are 10%, 5%, and 3% for the polycrystalline [Fig. 6(A), low doping density [Fig. 6(C)] ceramic and high doping density [Fig.6(B)] ceramic samples, respectively. The better slope efficiency of the lower doped ceramic is due to the poor optical quality of the highly doped ceramic sample. Maximum output energy for each ceramic sample reached 2 mJ. This data shows that reasonable efficiencies can be achieved using hot-pressed ceramic crystals in comparison with thermally diffused samples.

4. Conclusions

The reported fabrication process of an optical material based on hot-pressed Cr^{2+}:ZnSe ceramic with an optical quality was sufficient for the first demonstration of gain-switched lasing in the mid-IR. The ceramic laser yielded 2 mJ of output energy at a slope efficiency of up to 5%. Further investigations are needed to continue the development of hot-pressed samples with high optical density (k=5-10 cm^{-1} at 1.8 µm) and high optical transparency.

The presented results demonstrate the first ever hot-pressed ceramic Cr^{2+}:ZnSe laser system operating in the middle infrared as well as proof that the mid-IR laser systems based on hot-pressed ceramics have a promising future. These results are the stepping-stones to further technological advances in raising the pump absorption and decreasing the passive losses in hot-pressed ceramics. When these goals are met hot-pressed ceramics will make a large impact on the synthesis of large-scale mid-IR lasers.

With an improvement in the laser cavity the existing hot-pressed ceramic laser systems could yield much higher slope efficiencies as well as output energies. The existing mirrors that are available in the mid-IR are not able to withstand the high-energy short pulse radiation

used as a pump source. Once new technologies are developed with respect to mid-IR laser mirrors different cavity designs such as longitudinal pumping can be used thus improving the output characteristics of these lasers tremendously.

Acknowledgments