Crystal field engineering of transition metal doped II-VI ternary and quaternary semiconductors for mid-IR tunable laser applications

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Abstract: We report on crystal-field engineering of solid-state laser gain media based on new transition metal (TM) (iron) doped II-VI ternary and quaternary semiconductor materials for middle-infrared (mid-IR) tunable laser applications. Novel ternary and quaternary TM:II-VI materials were fabricated in powder form using thermal annealing of mixtures of commercially available binary powders sealed in evacuated quartz ampoules. These resultant powders were characterized using XRD, micro-Raman spectroscopy, photoluminescence (PL) and PL kinetics. We demonstrate: 1) that this synthesis method enables laser active powder media and is an effective means to fabricate and prototype novel laser active materials, 2) by introducing heavier or lighter ions into the host crystal lattice, it is possible to independently engineer the spectral positions of the absorption and PL band of TM ions in II-VI crystals, and 3) the first time to our knowledge room temperature, mirrorless, random lasing of iron doped Zn$_{0.5}$Cd$_{0.5}$Te powders at 5.9 μm.

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References and links

Recent progress in lasers based on transition metal (e.g. Cr\textsuperscript{2+} and Fe\textsuperscript{2+}) doped II-VI semiconductors enables access to the 1.9-6.0 \( \mu \)m spectral region with a high efficiency, multi-Watt output power, tunability in excess of 1000 nm, and narrow spectral linewidth [1–5]. Regardless of the progress in mid-IR TM doped II-VI crystals and lasers several important issues are still outstanding. One of them is covering the spectral gap between the oscillation band of chromium and iron doped materials, ~3-4 \( \mu \)m. The tunabilities of chromium and iron doped Zn-chalcogenides stretch over 1.9-3.3 and 3.5-5.1 \( \mu \)m spectral ranges, respectively. Therefore, the development of new lasers materials with a maximum emission cross-section between 2.9 and 3.5 \( \mu \)m is essential to cover this gap. The second important research thrust is to extend tunability of TM:II-VI solid state lasers to longer wavelengths with a strategic goal to cover 1.9-10 \( \mu \)m spectral range. Another important issue is to control the absorption band spectral position of iron doped II-VI laser crystals. Several iron doped materials (for example Fe: CdMnTe [6]) are promising candidates for room-temperature (RT) lasers with tunability up to 6 \( \mu \)m; however, these crystals require a 3.5 \( \mu \)m pump source. There are no convenient direct laser sources around this wavelength at the moment. Therefore a shift of the absorption band to the shorter wavelength will allow using conventional 2.9 \( \mu \)m Er:YAG laser as a pump source. This study is primarily focused on compounds doped with Fe\textsuperscript{2+} ions. In this paper we report on a study of crystal field engineering of TM doped II-VI ternary and quaternary semiconductors (II-VI semiconductors composed of three and four different species of ions respectively) for mid-IR tunable laser applications. To reduce the cost of sample fabrication we used an approach based on synthesis of TM doped ternary and quaternary powders by thermal annealing. The fabricated compounds were analyzed by X-ray diffraction (XRD) and micro-Raman spectroscopy to verify whether the resulting powders were simply mechanical mixtures of binary powders or new ternary and quaternary compounds that could be used for prototyping properties of future crystals on their basis and used for fabrication of hot-pressed ceramic laser materials.

2. Spectroscopic properties of \textsuperscript{4}D ions

Energy structure of TM ions in II–VI compounds has been extensively studied since the 1960s (see, for example [7, 8]). The \textsuperscript{4}D ground states of Fe\textsuperscript{2+} (3d\textsuperscript{6}) and Cr\textsuperscript{2+} (3d\textsuperscript{4}) in the 1960s (see, for example [7, 8]).
The tetrahedral crystal field \((T_d)\) are split into the doublet \(5E\) and triplet \(5T_2\), respectively. Energy splitting between these levels in the tetrahedral coordination corresponds to the mid-IR spectral range and can be estimated using crystal field theory as [8]:

\[
\Delta = E(5E) - E(5T_2) = 10D_q = \left( \frac{20}{27} \right) \frac{Q^2}{4\pi\epsilon_0 a^5} \langle r^4 \rangle_{3d},
\]

where \(D_q\) is a crystal field parameter, \(Q\) is a ligand’s charge, \(a\) is a distance between ligands and transition metals, and \(\langle r^4 \rangle_{3d}\) is the mean radius of the 3d-electrons. The \(5T_2\) and \(5E\) are the two lowest states for a system with \(D_q/B < 1.2\), where \(B\) is Racah parameter [9]. The transitions between these levels are spin-allowed. All other transitions from \(5D\) levels are spin forbidden. The simple consideration of the crystal-field theory predicts that the energy splitting of the ground state \((\Delta E)\) of TM ions strongly depends on a distance \((a)\) between ligands and TM ions \((\Delta E \sim a^{-5})\). As a result, the TM ions in hosts with bigger lattice constants should have smaller energy splitting and demonstrate a “red shift” of absorption and emission bands. The electron-phonon coupling of the TM ions in the II-VI hosts results in significant broadening of absorption and emission bands as well as in strong Franck-Condon shift. According to a strong linear electron-phonon coupling with effective phonon \((\omega_{ph})\) approximation, the Stokes shift between absorption and emission band is given by [9]:

\[
\Delta E_{st} = (2S-1)\hbar\omega_{ph}
\]

where \(S\) is Huang-Rhys factor. Both energy level splitting (Eq. (1)) and strength of electron-phonon coupling (Eq. (2)) define spectral position of the absorption and emission bands of iron and chromium in II-VI binary, ternary and quaternary compounds. An additional parameter which could modify the energy level diagram is covalency of bonds in the lattice. All above parameters depend on the nature of bulk compounds. It makes II-VI ternary and quaternary semiconductors very attractive for broad-band lasers applications and opens a possibility for efficient control of the exact spectral location of absorption and emission bands of TM ions by changing the host composition [10–12].

3. Experimental details

Iron and chromium doped ternary and quaternary compounds \(\text{Cd}_{1-x}\text{Mn}_x\text{Te}, \text{Cd}_{1-x}\text{Mn}_x\text{S}, \text{Cd}_{1-x}\text{Mn}_x\text{Se}, \text{Cd}_{0.5}\text{Mn}_{0.5}\text{S}0.5\text{Se}0.5, \text{Zn}_{1-x}\text{Mn}_x\text{S}, \text{Zn}_{1-x}\text{Mn}_x\text{Se}, \text{Zn}_{0.5}\text{Mn}_{0.5}\text{S}0.5\text{Se}0.5, \text{Cd}_{2-x}\text{Zn}_x\text{Te}, \text{Zn}_{1-x}\text{Ca}_{1-x}\text{S}, \) with \(x = 0.5-0.25\), were prepared by using thermo-annealing technique. Briefly, the starting commercially available binary powders (Sigma Aldrich, Alfa Aesar) were mixed in the appropriate molar ratios, sealed in evacuated \((10^{-3}\) Torr) quartz ampoules, and annealed at high temperatures \((800-1000\) °C) for several days.

Absorption measurements were performed with the use of IR Prestige-21 (Shimadzu) FTIR spectrometer equipped with EasiDiff (Pike Technologies) attachment. The mid-IR PL spectra were collected with a 76 mm lens (CaF\(_2\)) and detected by Acton Research Spectra-Pro 300i Spectrograph combined with liquid nitrogen cooled HgCdTe detector (EGG Judson J15D) for Fe doped materials and PbS detector (Acton Research ID-442) for Cr doped materials. We have used a CW Er-fiber laser system operating at 1.53 \(\mu\)m (IPG ELR-20-1532.6-LP) and a Q-switched Er:Cr:YSGG laser operating at 2.78 \(\mu\)m with 65 ns pulse duration for excitation of Cr and Fe doped samples, respectively. Measurements were performed in a closed-cycle liquid helium cryostat under \(10^{-6}\) Torr at temperatures ranging from 13K to room temperature. Sample composition, integrity, and grain size were characterized by micro-Raman technique and X-ray diffraction (XRD). We performed Raman measurements using a Horiba Jobin Yvon LabRam HR Micro-Raman System equipped with 800 mm focal length spectrometer (HR 800 UV) optimized for the 200-1600 nm spectral region. We used a He-Ne laser operating at 632.8 nm for excitation with 6 mW (10 \(\times\)...
objective) incident power at the sample. XRD measurements on the nominally ternary and quaternary compounds were performed using our Philips X’pert diffractometer with Cu Ka radiation of 1.5418Å wavelength at scan speeds of 0.001–0.05°/s.

4. Results and discussion

Cd$_{1-x}$Mn$_x$S(Se) and Zn$_{1-x}$Mn$_x$S compounds

XRD measurements on nominally ternary Cd$_{1-x}$Mn$_x$S powders (Fig. 1(a)) established that these materials have hexagonal crystal structure clearly distinct from that of the starting powders (CdS: cubic zincblende; MnS: cubic rocksalt). Lattice constants vary substantially with the concentration of Mn in the system. Refinement of the crystal structure has yielded reliable values of the lattice constants. The values for lattice constants for this hexagonal material are shown in Fig. 1(b). Figure 1(b) combines data for the Cd-based compounds, with lattice constants for the corresponding Zn-based materials. The values for wurtzite CdS, MnS, and ZnS are also shown for comparison. For both $a$ and $c$, an approximate linear relationship, following Vegard’s law, is observed with varying Mn fraction across the entire Cd-Mn-Zn system. The comparative Raman spectra of ternary and quaternary compounds with ZnS and ZnSe are shown in Fig. 2(a). It can be seen that each compound has unique features in the Raman spectrum indicating again that ternary and quaternary Zn$_{0.75}$Mn$_{0.25}$S$_{0.25}$Se$_{0.75}$ powders are not a mechanical mixture of ZnS, MnS and ZnSe. The Raman spectrum of MnS is not shown since it has a strong fluorescence background under 632 nm excitation masking the weak Raman signal. These Raman mapping experiments have shown that: (1) Samples in this group also consisted of new ternary and quaternary compounds with concentration of any pure ZnS, ZnSe or MnS in the annealed samples below the limit of sensitivity of our measurement; and (2) Ternary and quaternary compounds were homogenous in terms of chemical composition with a high yield.

Fig. 1. A) XRD from Cd$_{0.75}$Mn$_{0.25}$S powder compared to XRD of corresponding starting powders (CdS and MnS); B) Effect of Mn addition on the lattice constant of the hexagonal structure of Cr: Cd$_{1-x}$Mn$_x$S and Cr: Zn$_{1-x}$Mn$_x$S.
In this study, powders were prepared with the same stoichiometry but annealed at either 925°C or 1000°C for comparison and within this range no dependence on annealing temperature was observed in the XRD patterns, as well as Raman and PL spectra. The PL spectra of Cr doped ternary Zn$_{1-x}$Mn$_x$S (x = 0.5, 0.25) and quaternary Zn$_{0.75}$Mn$_{0.25}$S$_{0.25}$Se$_{0.75}$ powder compounds obtained in the course of this study have not shown significant differences in terms of band position and width compared to binary Cr:ZnS and Cr:ZnSe respectively. On the contrary, the Fe doped compounds featured different PL spectra for binary, ternary and quaternary samples. The normalized experimental photoluminescence spectra of Fe doped powder binary, ternary and quaternary Zn chalcogenide samples are shown in Fig. 3(a) and Fig. 3(b). A dip at 4300 nm is caused by absorption of atmospheric CO$_2$. Comparing Fe:ZnS (curve i) with Fe:Zn$_{0.75}$Mn$_{0.25}$S (curve ii) and Fe:Zn$_{0.5}$Mn$_{0.5}$S (curve iv), as Mn concentration is increased the PL band of the samples are shifted to longer wavelengths and broadened. Similarly, comparing Fe:Zn$_{0.75}$Mn$_{0.25}$S (curve ii) with Fe:Zn$_{0.75}$Mn$_{0.25}$Se (curve v) and Fe:Zn$_{0.75}$Mn$_{0.25}$S$_{0.25}$Se$_{0.75}$ (curve vi) as sulfide, is mixed with selenide to form a quaternary compound, again the maximum of the PL is shifted to longer wavelengths and the emission band is broadened as disorder is increased. In the case of Fe:Zn$_{0.5}$Mn$_{0.5}$S as compared to Fe:ZnS, the PL maximum is shifted as much as 500 nm from 3900 to 4400 nm with that Fe:Zn$_{0.5}$Mn$_{0.5}$S shifted to even longer than Fe:ZnSe (curve iii). However, the wavelengths at maximum of PL spectra in all composite materials are shorter than 4.5 μm. Therefore in order to achieve luminescence longer than 5 μm, it is necessary to explore compounds with larger ions, such as CdSe and CdTe-based compounds.

Figure 3(c) shows the PL spectra of Fe: Cd$_{1-x}$Mn$_x$Se after a 3.5 μm filter for x = 0, x = 0.25 and x = 0.5. These are plotted along with the absorption features of CO$_2$ and water to more easily illustrate features of these spectra. The deep trough centered near 4300 nm is due to atmospheric CO$_2$. The prominent spikes centered near 5600 nm are artifacts caused by the second order of the Er:Cr:YSGG pump at 2788 nm. These spectra show a smooth shift toward longer wavelengths with the addition of Mn ions from x = 0 to x = 0.5. In addition, the disorder due to increased concentration of Mn appears to induce significant broadening of the PL spectrum as well as a shift of the wavelength of maximum PL by more than 500 nm.
Fig. 3. Normalized non-calibrated PL spectra of Fe:Zn$_{1-x}$Mn$_x$S$_{1-y}$Se$_y$ powder samples annealed at 925°C and 1000°C: A) Fe:ZnS (i), Fe:Zn$_{0.75}$Mn$_{0.25}$S (ii), Fe:ZnSe (iii), and Fe:Zn$_{0.5}$Mn$_{0.5}$S (iv) shown with the absorption of atmospheric CO$_2$ and H$_2$O (x); B) Fe:Zn$_{0.75}$Mn$_{0.25}$S (ii), Fe:Zn$_{0.75}$Mn$_{0.25}$Se (v), and Fe:Zn$_{0.75}$Mn$_{0.25}$S$_{0.25}$Se$_{0.75}$ (vi); C) Fe:CdSe (vii), Fe:Cd$_{0.75}$Mn$_{0.25}$Se (viii), and Fe:Cd$_{0.5}$Mn$_{0.5}$Se (ix) powders annealed at 925°C measured after a 3 μm filter. The prominent peak centered near 5.6 μm is the second order of the pump wavelength of 2.79 μm.

Figure 4(a) shows the low temperature kinetics of PL on a log scale for Fe:CdMnSe (curve v and vi). For kinetics measurements, powders were sealed in ZnSe cuvettes and installed in a cryostat at 10$^{-6}$ Torr and measured from room temperature to 13K. As can be seen in the Fig. 4, the rate of decay is still changing from 15 μs at 45K to 20 μs at 13K, indicating that the quantum efficiency does not reach 100% at 13K. There may still be significant quenching at low temperature, as has been observed in Fe:ZnS which has a lifetime of approximately 5 μs at 13K while radiative lifetime was estimated to be 55 μs [16]. The low temperature lifetime of Fe:CdMnSe is longer than that of Fe:ZnS, but still significantly shorter than the low temperature PL lifetime of Fe:ZnSe (55 μs). This shortening of the lifetime is possibly due to non-radiative quenching [13]. Figure 4(b) curve ii shows room temperature kinetics for Fe:Cd$_{0.75}$Mn$_{0.25}$Se. As compared to Fe:ZnSe (curve v), all compounds show some amount of quenching of the lifetime at room temperature, but in the case of Fe:Cd$_{0.75}$Mn$_{0.25}$Se, the lifetime is quenched so strongly it falls within the resolution of the detector (<50 ns).

Cd$_x$Mn$_{1-x}$Te and Zn$_x$Cd$_{1-x}$Te compounds

Iron doped nominally ternary compounds of Cd$_x$Mn$_{1-x}$Te were produced by annealing mixtures of CdTe and MnTe in sealed quartz ampoules. The relative amounts of CdTe and MnTe were chosen to produce samples of Cd$_x$Mn$_{1-x}$Te with x = 0.50 and x = 0.75. Similarly, samples of Cd$_x$Mn$_{1-x}$Se were prepared with x = 0.5 and x = 0.75. All samples annealed in the 875-925°C range were solids with polycrystalline appearance. The grain sizes were substantially larger than those of the initial starting materials, clearly indicating a significant grain growth during annealing.

XRD measurements of the Fe doped nominally ternary Cd$_{1-x}$Mn$_x$Te compound and the corresponding starting powders are depicted in Fig. 5. The starting CdTe powder used for preparation of this compound has the zinc blende structure and its XRD pattern is shown at the bottom of Fig. 5. The starting powder used for MnTe was predominantly a hexagonal
material in the ideal NiAs structure. However, this starting powder also contained significant amounts of MnTe₂, which crystallizes in the cubic pyrite structure. The prominent (211) pyrite peak is marked with (+) in Fig. 5. In addition, a small amount of wurtzite MnTe may also have been present as evidenced by some weak wurtzite peaks (not marked in Fig. 5). The XRD patterns for the nominally ternary Cd₁₋ₓMnₓTe powders index perfectly to the cubic zinc blende structure. The positions of the Bragg reflections of the cubic peaks are clearly shifted with respect to those of pure CdTe. In agreement with the Raman data, these shifts establish the formation of the ternary alloy Cd₁₋ₓMnₓTe with Mn incorporation in the CdTe lattice, which leads to changes in unit cell dimensions. These changes are shown in Fig. 5(b). The unit cell with a = 6.4800 Å of CdTe is reduced by 1.2% as the concentration of Mn increases from 0 to 50% in the alloy. Since MnTe is not known to crystallize in the zinc blende structure, no comparison data is available for x = 1. The linear trend for x > 0.5 is shown as a dashed line because it constitutes an extrapolation from our explored concentration range from x = 0 to x = 0.5. The changes in the lattice constant of Cd₁₋ₓMnₓTe as a function of the Mn concentration x correspond to changes in cation-anion distance in the crystal. Cation-anion distance is relevant as it represents the actual separation between the mid-IR active impurity (Fe²⁺ in this case) and its ligand in the host crystal.

We have observed a fairly strong Fe²⁺ RT PL under 2.78 µm excitation. Figure 6 shows normalized non-calibrated experimental PL spectra of Fe:CdₓMn₁₋ₓTe after a 3.5 µm filter for x = 0, x = 0.25 and x = 0.5 obtained under the same experimental conditions. Again, these are shown along with the absorption of atmospheric CO₂ and water (curve iv) to illustrate that the origin of the deep trough centered at 4.3 µm is due to CO₂ absorption and the apparent peak near 6300 nm is caused by a window of transparency in the absorption of atmospheric water. The prominent spikes centered near 5600 nm are artifacts caused by the second order of the Er:Cr:YSGG pump at 2788 nm. The maximum wavelengths of these spectra show a smooth shift of 400-500 nm toward longer wavelengths with the addition of Mn ions from x = 0 to x = 0.5.

As can be seen, the Fe:Cd₀.₅Mn₀.₅Te PL band (curve iii) is slightly wider and shifted by about 200 nm to longer wavelengths with respect to the PL band from Fe:CdTe (curve i). Unlike in the case of Fe:CdₓMn₁₋ₓSe, an increased concentration of Mn does not appear to induce significant shifting or broadening of the PL spectrum. While some small trend of broadening and red-shifting is evident, differences in these PL spectra are near the level of error in the measurement.
Fig. 5. A) XRD from Cd$_{1-x}$Mn$_x$Te powder compared to XRD of corresponding starting powders (CdTe and MnTe + MnTe$_2$); B) Effect of Mn addition on the lattice constant “a” of the zinc blende structure of Fe:Cd$_{1-x}$Mn$_x$Te. Linear trend for $x > 0.5$ is shown as a dashed line.

Fig. 6. Non-calibrated, normalized PL spectra of i) Fe:CdTe, ii) Fe:Cd$_{0.75}$Mn$_{0.25}$Te and iii) Fe:Cd$_{0.5}$Mn$_{0.5}$Te powders annealed at 925°C measured after a 3.5 $\mu$m filter, shown with iv) atmospheric absorption features. The apparent peak near 6.3 $\mu$m is caused by a window of transparency in the absorption of atmospheric water.

Figure 7 shows absorption and emission spectra of iron doped ZnTe, CdTe, and Cd$_{0.5}$Zn$_{0.5}$Te samples. As one can expect from the simple crystal field approximation, the smaller crystal-field splitting in CdTe samples (in comparison with ZnTe host) results in shift of the absorption and emission bands of the iron ions to longer wavelength. It makes cadmium compounds very attractive for laser oscillation with wavelength longer than 6 $\mu$m. However, a shift of the absorption band toward longer wavelengths in the cadmium compounds results in its poor overlap with oscillation wavelengths of commonly used Er pump lasers (dashed line in Fig. 7(a)). As one can see from the Fig. 7, the Stokes shift in the Fe:Zn$_{0.5}$Cd$_{0.5}$Te mixed sample is larger than in binary compounds. Therefore, on one hand, the absorption spectrum of the Fe:Zn$_{0.5}$Cd$_{0.5}$Te nicely overlaps with Er pump laser wavelength...
(similar to Fe:ZnTe sample); and on the other hand, the emission band is shifted to the longer wavelength (similar to Fe:CdTe sample). A similar effect was reported for Cr:ZnS,Se$_{1-x}$ crystals [14] and could be explained by a stronger electron phonon coupling in the mixed crystals.

Figure 4(a) shows the low temperature kinetics of PL on a log scale for Fe:CdTe (curves i and ii), and Fe:ZnCdTe (curves iii and iv). As with Fe:Cd$_{0.75}$Mn$_{0.25}$Te, Fe:CdTe and ZnCdTe powder samples were sealed in ZnSe cuvettes and mounted in a cryostat. Fe:CdTe powder demonstrated non-exponential behavior in the beginning, however, the luminescence kinetics asymptotically approach exponential behavior over a short time so the lifetime can be measured by the tail-fitting method. This non-exponential behavior is most likely due to non-radiative energy migration between iron ions becoming more dominant at lower temperatures. One can see from the Fig. 4(a) that the rate of decay of the PL signal of Fe:CdTe does not change much between 40K (68 μs) and 14K (75 μs), so it can be assumed that at this temperature, quantum efficiency approaches 100% and the lifetime at low temperature is approximately equal to the radiative lifetime. A lifetime of 75 μs was measured for Fe:Cd$_{0.55}$Mn$_{0.45}$Te single crystal and previously reported in [6]. The measured low temperature lifetime of 75 μs agreed very well with these previously reported results. In the case of Fe:ZnCdTe, there is a clear non-exponential behavior, however, the kinetics asymptotically approach an exponential with a decay rate that shows little change between 40K and 14K, so by using the tail-fitting method, the radiative lifetime was estimated at 72 μs.

Fig. 7. Absorption (A) and photoluminescence (B) spectra of Fe:ZnTe (i), Fe:CdTe (ii), and Fe:Cd$_{0.5}$Zn$_{0.5}$Te (iii) sample; random lasing spectra (iv) of Fe:Cd$_{0.5}$Zn$_{0.5}$Te at room temperature (excitation wavelength 2.78 μm).

**Optical gain in iron-doped compounds**

The PL spectra were used to calculate the gain profiles using the Fuchtbauer-Ladenburg equation [15],

$$\sigma_{em}(\lambda) = \frac{\lambda^2 I(\lambda)}{8\pi cn^2 \tau_{rad} \int I(\lambda) \lambda d\lambda},$$

where $\sigma_{em}(\lambda)$ is the emission cross-section, $\lambda$ is emission wavelength, $n = 2.7$ is the refractive index, $c$ is the speed of light, $\tau_{rad}$ is the radiative lifetime, and $I(\lambda)$ is the emission spectrum calibrated with respect to the detection platform.
In low-doped Fe:ZnSe, radiative lifetime was measured at low temperature to be approximately 55 μs and Fe:ZnS was estimated [16] to have a similar lifetime of 50 μs. Fe:CdTe shows a stable lifetime below 40 K of approximately 72 μs which is close to the lifetime of Fe:CdMnTe of 75 μs reported in [6], therefore in our calculations for CdTe based compounds radiative lifetimes around 72 μs were used. In the case of Fe:CdMnSe, measured lifetimes at low temperature were still strongly quenched, and without more extensive quantum efficiency studies of low-doped samples, it is difficult to pinpoint the radiative lifetime. However, it is reasonable to assume that the radiative lifetime for Fe:CdSe based compounds would fall within the range of those of Fe:ZnSe and Fe:CdTe compounds. Therefore, for these calculations, the range 55-77 μs was used as limits on radiative lifetime of Fe:CdMnSe.

Figure 8 shows the normalized cross-sections of emission for studied samples calculated from calibrated photoluminescence measurements. Lifetime measurements affect only the amplitude of these gain profiles, so the shapes of these curves are dependent only on PL spectra. PL spectra of Fe:CdMnSe, as well as Fe:CdTe, Fe:CdMnTe, and Fe:ZnCdTe were measured with the use of 3 and 3.5 μm filters, respectively. We used dashed lines for normalized cross-sections in Fig. 8 to indicate that above 6 μm for Fe:CdMnSe, and above 7 μm for Fe:CdMnTe and Fe:ZnCdTe, there is a lack of confidence in experimental data due to possible input of second order diffraction of PL signal. As one can see from the Fig. 8, these compounds effectively cover the spectral range over 3-8μm. It should be noted that the gain profiles of Fe:Zn0.5Cd0.5Te and Fe:Cd0.5Mn0.5Te match one another nearly to within measurement error and overlap strongly with the emission of Fe:CdTe, so each of these compounds offers emission covering similar spectral regions but can have very different absorption bands as shown in Fig. 7.

Table 1 lists spectroscopic characteristics for these samples based on PL and lifetime measurements including the magnitude (σ_max) and spectral position (λ_max) of the maximum of the emission cross-sections, the spectral width of the gain profiles (Δλ), and the room temperature luminescence lifetimes (τ_RT). In general, it shows that the gain profiles of disordered compounds are broader and that by changing both the crystal field and the disorder in the host crystal it is possible to induce “red shift” in λ_max.

![Normalized calculated cross-sections of emission for Fe:ZnS, Fe:ZnSe, Fe:Cd0.75Mn0.25Se, Fe:CdTe, Fe:Zn0.5Cd0.5Te, and Fe:Cd0.5Mn0.5Te. Dashed lines indicate low confidence data that may be perturbed by a possible second order diffraction of PL signal.](image-url)
Table 1. Spectroscopic properties measured for materials prepared for this study.

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<th>Material</th>
<th>$\sigma_{\text{norm}} \text{ max} \text{ (cm}^2\text{)}$</th>
<th>$\lambda_{\text{max}} \text{ (\text{\mu}m)}$</th>
<th>$\Delta\lambda \text{ (\text{\mu}m)}$</th>
<th>FWHM</th>
<th>$\tau_{\text{RT}} \text{ (ns)}$</th>
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<td>$1.1 \times 10^{-18}$</td>
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Values denoted with a "*" are based on radiative lifetime estimates rather than direct measurement and need to be verified with further study.

Good overlap of the absorption band with a pump wavelength enabled a high optical gain and resulted in realization of random lasing of the Fe:Zn$_{0.5}$Cd$_{0.5}$Te powder. Random oscillation is based on laser active scattering media without any cavity as well as other optical elements. The positive laser feedback arises due to photon scattering in the gain media. Early, random lasing of the chromium doped II-VI powers was demonstrated in [14, 17, 18].

In our experiments, we observed two basic features of the random lasing of the Fe:Zn$_{0.5}$Cd$_{0.5}$Te powder: threshold-like dependence of the output signal; and strong spectral line narrowing above the laser threshold. Figure 7(b) shows spectra of the Fe:Zn$_{0.5}$Cd$_{0.5}$Te powder below (curve iii) and above (curve iv) laser threshold. As one can see from Fig. 7, the bandwidth of the PL signal decreases from 3000 nm to ~70 nm with the emission spectrum centered at 5.9 $\mu$m. It should be noted that optical gain band is shifted to the longer wavelength with respect to the spontaneous emission according to Fuchtbauer–Ladenburg equation. This predicted shape of the gain band is in agreement with the spectral placement of the random lasing emission shown in Fig. 7 corresponding approximately with the maximum gain, possibly with a small shift toward shorter wavelength. These experiments demonstrate that Fe:Zn$_{0.5}$Cd$_{0.5}$Te gain material is very promising for mid-IR tunable lasing with wavelength longer than 6 $\mu$m.

5. Conclusions

The X-ray diffraction and Micro-Raman mapping experiments have shown homogeneous composition of the samples corresponding to the new ternary and quaternary compounds that were formed by a simple annealing. In addition to producing ternary II-VI materials with variable concentration of the second cation (Mn, Ca, Zn), we simultaneously doped these new compounds with iron. These results allow us to make two important statements: (1) It is possible to produce ternary and quaternary II-VI materials doped with TM ions by simple annealing of the commercially available binary powders omitting expensive and complicated crystal growth processes, (2) It is possible to effectively shift absorption and PL of TM in II-VI host materials towards shorter or longer wavelength by varying composition, type and amount of the second cation in ternary II-VI materials. Iron doped Zn$_{1-x}$Cd$_x$Te active powders are very attractive for tunable lasing with a wavelength longer than 6 $\mu$m. We report for the first time to our knowledge a random lasing regime of Fe:Zn$_{0.5}$Cd$_{0.5}$Te powders at 5.9 $\mu$m.

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