Introduction
The demand for middle infrared (mid-IR) lasers operating at room temperature is growing as there are many applications including non-invasive medical diagnostics, molecular spectroscopy and infrared countermeasures. Fe:ZnSe can operate over a broad spectral range in the mid-IR, 3.6-5.2 µm, but there are no convenient pump sources available. One potential method of pumping Fe:ZnSe efficiently is through energy transfer from another transition metal. In this project, we studied the energy transfer of Cr:ZnSe to Fe:Cr:ZnSe through kinetics and photoluminescence measurements. We also report on photorefractive effects in II-VI metal doped semiconductors, which could be used for the fabrication of waveguides and holographic gratings in the mid-IR.

Goals
• Study the energy transfer process in Fe-Cr codoped ZnSe materials to developed more efficient and convenient pump sources for mid-IR Fe:ZnSe lasers
• Study photorefractive effects in doped II-VI semiconductor materials for possible applications such as holographic gratings and waveguide fabrication devices for the mid-IR spectral region

Absorption and Emission Spectra

Photoluminescence Experimental Setup

- IPG Photonics 1.56µm Er-fiber laser
- Spectra Pro 300i spectrometer
- Lock-in amplifier

Figure 2. Photoluminescence experimental scheme

Photoluminescence Results

The non-linear curve indicates that there are multiple exponential functions describing the relaxation of excited ions. The energy transfer rate depends on the donor-acceptor distance. A non-exponential decay curve is produced when the separation varies.

Kinetics Experimental Setup

- D_2: Raman shifted Nd:YAG 1.56µm
- Tektronix TDS 744A oscilloscope
- VIGO System S.A. PVI-3TE-6 detector

Figure 3. Photoluminescence of Fe:Cr:ZnSe [I], Cr:ZnSe [II] crystals under 1.56µm excitation

Kinetics Results

The largest observed change in the refractive index was 1.12, which occurred in Cr:ZnSe. The intensity of luminescence from Cr:ZnSe was 12 times larger than the luminescence of Fe:Cr:ZnSe, with equal concentration of Cr^{2+} ions for each crystal, indicating energy transfer from chromium to iron.

The experimental setup is shown in Figure 2.

Table 1. Absorption and Emission Spectra of Cr:ZnSe and Fe:Cr:ZnSe crystals

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Cr Concentration</th>
<th>Fe Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe:Cr:ZnSe</td>
<td>2.5 x 10^{23} cm^{-3}</td>
<td>9.0 x 10^{23} cm^{-3}</td>
</tr>
<tr>
<td>Cr:ZnSe</td>
<td>2.5 x 10^{23} cm^{-3}</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Figure 4. Kinetics laser system

Figure 6. Refractive index modification optical scheme

Conclusions

- Energy Transfer
  • The kinetics of photoluminescence provide evidence that there is fast Cr-Fe energy transfer and the transfer was measured to be 290ns
  • Theoretical calculations using the Förster-Dexter model indicate that the energy transfer rate could be as high as 1/250ps
- Refractive Index Modification
  • To achieve more effective refractive index modification through the described methods for metal doped II-VI semiconductors, radiation at a stronger absorption wavelength may be required and the parameters described must be optimized

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References


Förster Energy Transfer

Förster resonance energy transfer is a non-radiative energy transfer process between an excited donor and acceptor through dipole-dipole coupling. The following equation was used to estimate the chromium-ion energy transfer in Fe:Cr:ZnSe.

Energy Transfer Rate

\[ W_{DD}^{FE} = \frac{4\pi R_0^2}{3} \left( \frac{1}{4\pi\epsilon_0} \right)^{3/2} \left( \frac{\mu_1 \mu_2}{2m_e} \right)^{2} \int \sigma_{D} E_{D} E_{A} d\Omega \]

where \( R_0 \) is the refractive index, \( a \) is the central frequency, \( m \) is electron mass, \( R \) is the ion-ion separation distance, \( \sigma_{D} \) and \( \sigma_{A} \) are form factors.

Oscillator Strength

\[ f_d = \left( \frac{4\pi e^4}{3(2m_e)^2} \right) \int \sigma_{D} E_{D} E_{A} d\Omega \]

\[ f_a = \left( \frac{4\pi e^4}{3(2m_e)^2} \right) \int \sigma_{A} E_{D} E_{A} d\Omega \]

\[ W_{DD}^{FE} = \frac{1}{250 \text{ps}} \text{ @ } R=0.4 \text{nm} \]

Crystal Polishing

- 240 grit for bottom surface to scatter unwanted reflection
- 1200 grit silicon carbide paper for exposed surface

Power Meter

• Ophir power meter
- 2mm beam diameter
• IPG Photonics Er-fiber laser
- 1.56µm

Figure 5. Kinetics of Fe^{2+} ions in Fe:Cr:ZnSe under 1.56µm excitation with a 3.5µm longpass filter

Figure 8. Refractive index of ZnSe [I] and Cr:ZnSe [II] as a function of time under 532nm radiation with a power density of 100 mW/cm^2

Table 1. Crystals Used in Experimental Work