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High-temperature solution growth of Cr^{2+} : CdSe for tunable mid-IR laser application

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Abstract

Solid-state tunable laser sources in the mid-IR region have been recently investigated for their potential in remote sensing applications. Room temperature lasers based on single crystals of chromium-doped CdSe are particularly interesting due to their broad band tunability beyond 2 μm spectral region. In this study, we have grown doped single crystals by the high-temperature gradient freezing solution technique, using selenium as the solvent. Crystals of 1.2 cm in diameter and up to 7 cm long, cracks and precipitates free could be obtained. The effective segregation coefficient of Cr^{2+} ions along the ingot was evaluated. Room temperature emission lifetime values of 3.0–4.5 μs were measured. © 2000 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

Cr^{2+} : CdSe has been shown [1,2] to be a promising room temperature solid state tunable mid-IR laser material, for remote sensing, environmental monitoring, and surgical applications. MacKay et al. [1] have demonstrated a continuous wavelength (cw) tunability over the 2.3–2.9 μm spectral region. They further reported that their mirror reflectivity was the only limit in this tunability range. Cr^{2+} : ZnSe was proven earlier [3,4] to lase in the 2.0–3.0 μm spectral region. Unfortunately, high concentrations ($> 5 \times 10^{18} \text{ cm}^{-3}$) of Cr^{2+} ions in-

crease the optical self-absorption observed beyond 2.0 μm [5]. For mid-IR laser applications, this absorption induces optical losses that limit the laser performance. Cr^{2+} : CdSe may not have this problem. Thus, high optical gains could be expected. Mid-IR absorption experiments on heavily doped CdSe are needed to confirm that.

Up to the present, the vapor transport and the melt have been the only techniques applied in growing chromium-doped CdSe. The first as reported by Schepler et al. [6] gave a single crystal unfortunately with a low doping efficiency. The second was reported by the same authors to produce polycrystals that cracked due to the anisotropic thermal expansion of CdSe. The thermal diffusion of chromium in pure CdSe is an interesting technique where the doping efficiency depends on the appropriate diffusion temperature and time.

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The undoped CdSe crystals used for diffusion experiments are generally grown from the vapor, the melt or from the solution [7–9].

The temperature gradient solution growth technique with selenium as the solvent was previously used to grow undoped medium resistivity ($\sim 10^6 \Omega \text{ cm}$) n-type single crystals of CdSe for nuclear radiation detection applications [9]. We have applied this method, slightly modified, for the same case of CdSe crystals, but doped with chromium. Compared to the melt growth, this technique has the advantage that the relatively reduced growth temperatures result in low dislocation densities and low contamination from the container. Furthermore, the solvent purifies the ingot. There have been numerous reports on segregation during the solution growth of bulk semiconductor crystals [10–15], describing the effects on the axial homogeneity of grown ingots. The effective segregation coefficient varies from one chemical element to another. It furthermore depends on the growth technique, and the experimental conditions.

In the present study, we describe the gradient freezing solution growth (GFSG) technique used to produce $\text{Cr}^{2+} : \text{CdSe}$. The structural quality of the crystals is presented, the concentration of Cr^{2+} along the ingot is evaluated from absorption spectroscopy and the effective segregation coefficient is calculated. Preliminary emission lifetime values are also given.

2. Experimental details

2.1. Growth of single crystals by the gradient freezing solution technique

Electronic grade CdSe powders purchased from General Electric (Chemical Electronic) were used as source material for the experiment. Prior to the growth, the powders were purified by a complete sublimation–crystallization process at 800°C under a dynamic vacuum in a clean and pre-baked long quartz ampoule. An amount of selenium (5N from Alfa), calculated from the reaction of dissolution of CdSe in Se and the Cd–Se phase diagram, was loaded in a quartz ampoule (12 mm ID and 14 mm OD), with a conical end. Our experi-

mental temperatures were chosen in the $1140\text{--}1160^\circ\text{C}$ range. A given amount of the sublimed CdSe, crushed in small parts and mixed up with powders of CrSe 99.5% (from Alfa), was placed on top of the selenium. The filled ampoule was evacuated to 10^{-6} Torr for about 12 h before it was sealed off.

The sealed ampoule was placed in a vertical single zone furnace, with its conical tip located in a $8^\circ\text{C}/\text{cm}$ temperature gradient. For a typical run, the temperature of the furnace was raised at a rate of $1^\circ\text{C}/\text{min}$ to 600°C where it was kept for 12 h, then it was slowly ($0.5^\circ\text{C}/\text{min}$) brought to 1160°C and kept there for five days. At this stage, the charge should be completely liquid. To initiate the growth, the temperature was slowly ($0.01^\circ\text{C}/\text{min}$) reduced to 1050°C where it was held for two days; then to 800°C at a rate of $0.05^\circ\text{C}/\text{min}$, and held there for two more days. Finally, it was brought to 30°C at a rate of $0.2^\circ\text{C}/\text{min}$. The ingot was removed from the ampoule. The selenium solvent was generally located at the upper (last to freeze) region of the ingot. All the ingots grown in our laboratory were single crystal except for the Se-rich region.

2.2. Characterizations

A diamond-coated wire saw was used to slice the ingot in the direction perpendicular to the growth axis. It should be noted that CdSe cleaves easily along this axis. The slices were optically polished and cleaned with trichloroethylene and acetone. The optical transmission microscopy was performed with a MEIJI microscope, coupled to a CCD camera that was connected to a computer for the image capture and processing. For the absorbance measurements, Fourier-transformed infrared spectroscopy was carried out with a computer-controlled MIDAC FT-IR spectrometer, in the $1.3\text{--}25 \mu\text{m}$ spectral region. Lifetime measurements were performed under excitation with the $1.91 \mu\text{m}$ output of a hydrogen Raman shifter, pumped by the $1.06 \mu\text{m}$ output of a Nd : YAG picosecond pulsed laser. An InAs fast photodiode and a computer-interfaced digital oscilloscope were used to detect and collect the Cr^{2+} luminescence signal. A $2 \mu\text{m}$ cut-off wavelength long pass filter placed in front of the detector was used to remove from

the detected light any scattered 1.91 μm pump beam.

3. Results and discussion

3.1. Transmission optical microscopy

Fig. 1 presents a micrograph of a $\text{Cr}^{2+}:\text{CdSe}$ sample grown by the gradient freezing solution technique. One can see a good structural homogeneity. Furthermore, unlike crystals obtained from the melt, no cracks or selenium precipitates are noticeable.

3.2. Mid-IR optical absorption

Chromium substitutes for cadmium atoms in the CdSe lattice, and can be in a neutral state, as well as in an oxidized state. A typical room temperature (300 K) mid-infrared optical absorption spectrum of $\text{Cr}^{2+}:\text{CdSe}$ in the 1.5–3.5 μm spectral region is illustrated in Fig. 2. The peak at 1.9 μm corresponds to the intracenter transition ${}^5\text{T}_2 \rightarrow {}^5\text{E}$ of Cr^{2+} in CdSe [16]. Its strength depends on the amount of Cr^{2+} ions contained in the sample. The

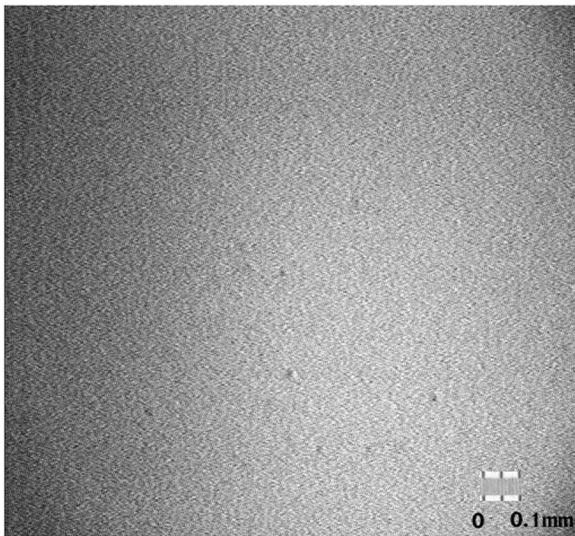


Fig. 1. Optical transmission micrograph of a $\text{Cr}^{2+}:\text{CdSe}$ sample cut perpendicular to the axis of an ingot grown by the gradient freezing solution technique.

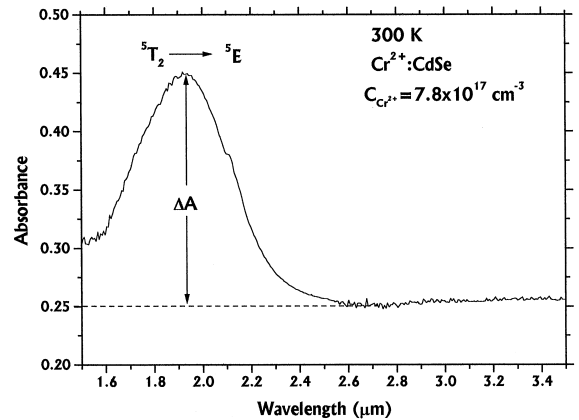


Fig. 2. Room temperature mid-infrared absorbance of a $\text{Cr}^{2+}:\text{CdSe}$ sample cut perpendicular to the axis of an ingot grown by gradient freezing solution technique. The concentration of chromium ions calculated is $7.8 \times 10^{17} \text{ cm}^{-3}$. The initial amount of chromium in the charge was equivalent to 1000 ppm ($1.8 \times 10^{19} \text{ atoms cm}^{-3}$).

average Cr^{2+} concentration is calculated by applying the Beer–Lambert’s law, and the following relation was used:

$$\Delta A = \sigma_a N \delta, \quad (1)$$

where ΔA is the absorbance (cf. Fig. 2), σ_a is the absorption cross section of the absorbing species; it has a value of $3 \times 10^{-18} \text{ cm}^2$ for Cr^{2+} in CdSe [6], N is the average concentration of the absorbing species and δ is the sample’s thickness.

3.3. Axial distribution of Cr^{2+} and calculation of the effective segregation coefficient

Fig. 3 depicts the axial distribution of Cr^{2+} ions in a chromium-doped CdSe ingot. The opened circles represent the concentration calculated from the absorption spectra, and the solid line, the theoretical concentration that will be discussed in this section. The concentration of Cr^{2+} ions decreases from the first-to-freeze to the last-to-freeze regions of the ingot, covering the 1.0×10^{18} – $1.5 \times 10^{17} \text{ cm}^{-3}$ range. This suggests that the effective segregation coefficient of Cr^{2+} here is greater than one. Since the initial amount of chromium in the charge was equivalent to 1000 ppm

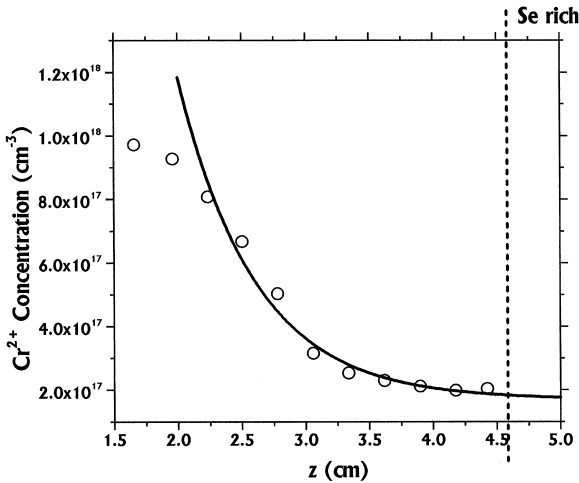


Fig. 3. Axial distribution of Cr²⁺ ions in a Cr²⁺ : CdSe ingot grown by a gradient freezing solution technique. The solid line represents the solution zone Pfann’s segregation model, for $k_{\text{eff}} = 7.8$, $C_o = 1.7 \times 10^{17} \text{ cm}^{-3}$, $C_L^o = 3.6 \times 10^{18} \text{ cm}^{-3}$, and $\delta_e = 4.7 \text{ cm}$.

($1.8 \times 10^{19} \text{ atoms cm}^{-3}$), we can therefore conclude that the chromium atoms incorporated in the CdSe host are not all in their second oxidation state, Cr²⁺. This is moreover strengthened by the electrical compensation observed from the resistivity measurements. We should recall that undoped CdSe is a “n”-type semiconductor and the highest resistivity measured does not exceed 10⁶ Ω cm. We could however measure resistivities as high as 10¹² Ω cm in chromium-doped CdSe. This results from the electrical compensation that can only occur in materials containing additional acceptor impurities. In chromium-doped CdSe, Cr²⁺ ions are electrically neutral, whereas Cr¹⁺ and Cr⁰ are singly and doubly charged acceptors, respectively, that can compensate the residual donors [16]. This explains the reason why not all the chromium atoms incorporated in CdSe contribute to the optical absorption of the material.

In order to evaluate the effective segregation coefficient (k_{eff}) of Cr²⁺, we have somewhat simplified the problem by assuming that: (i) The exchanges between the liquid and the solid phases take place within a constant volume $V_e (=S\delta_e)$. (ii)

The interfaces are flat. (iii) We are in a stationary state. (iv) Chromium exists in the liquid phase in its neutral and oxidized states. The balance equation in the volume V_e can then be written as

$$d(C_L V_e) = (C_o - C_S) dV. \tag{2}$$

C_L , C_o , and C_S are, respectively, the concentration of Cr²⁺ ions in the volume V_e , in the liquid beside V_e , and in the crystallized material, dV is the crystallized volume, when the variation of the position of the interfaces is dz . Considering that the concentration in V_e at the beginning of the crystallization ($z = 0$) is C_L^o , and recalling that $k_{\text{eff}} = C_S/C_L$, the solution to Eq. (2) can then be written as follows:

$$C_S(z) = C_o - (C_o - C_L^o k_{\text{eff}}) \exp\left(-\frac{k_{\text{eff}}}{\delta_e} z\right). \tag{3}$$

This is the Pfann’s solution segregation function. z is the axial position along the ingot. k_{eff} , C_o and C_L^o could be calculated by least-squares fitting. The best fit in Fig. 3 is obtained for $k_{\text{eff}} = 7.8$, $C_o = 1.7 \times 10^{17} \text{ cm}^{-3}$, and $C_L^o = 3.6 \times 10^{18} \text{ cm}^{-3}$, with $\delta_e = 4.7 \text{ cm}$.

Preliminary values of room temperature 2.0–2.9 μm emission lifetime vary between 3.0 and 4.5 μs, and seem not to depend strongly on the Cr²⁺ ions’ concentration considered within the range (cf. Fig. 3) studied in this report.

4. Conclusions

Single crystals of Cr²⁺ : CdSe were successfully grown by the gradient freezing solution technique, using selenium as the solvent. These crystals were free of cracks and selenium precipitates. The axial distribution of Cr²⁺ led to the conclusion that by substituting for Cd in the CdSe lattice, chromium is not only incorporated as electrically neutral Cr²⁺ ions, but also as singly charged Cr¹⁺ or doubly charged Cr⁰ acceptors. Moreover, an effective segregation of 7.8 was obtained from a numerical fit of the axial distribution of Cr²⁺ ions to the Pfann’s solution zone model. Preliminary values of room temperature emission lifetime varied between 3.0 and 4.5 μs.

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