

**GROWTH, SPECTROSCOPY AND PHOTOREFRACTIVE INVESTIGATION OF
VANADIUM DOPED CdSSe**

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We present two-wave mixing results obtained with a $\text{CdS}_{0.8}\text{Se}_{0.2}:\text{V}$ crystal. The $\text{CdS}_{0.8}\text{Se}_{0.2}:\text{V}$ crystal was grown by physical vapor transport (PVT) along with a concentration of 150 ppm (nominal) vanadium for creating trap centers. The as-grown crystal has a large crystal size, good optical quality, and a medium resistivity of 10^6 - 10^8 $\Omega\text{-cm}$. A large photorefractive gain coefficient of 0.24 cm^{-1} was observed at 633 nm with an optical intensity of 60 mW/cm^2 and a grating period of 1.6 μm . To our knowledge, this is the first observation of the photorefractive effect in a vanadium doped CdSSe crystal. Room temperature absorption and low temperature photoluminescence spectroscopy measurements are also discussed. With a significant photorefractive effect, the CdSSe:V crystals are promising for device applications based on photorefractive effect, in the wavelength range of 600-700 nm.

Introduction

Photorefractive materials are nonlinear optical materials which experience a significant change in the refractive index when exposed to inhomogeneous illumination. These materials have potential device applications in optical signal processing and related areas, including reversible holographic storage, tracking filters, optical interconnects, etc. Photorefractive crystals are being used to record the holographic interconnections between the neurons in optical neural networks. The optical implementation of artificial neural networks are useful in solving problems such as pattern recognition and robotics. Semiconductor crystals such as CdTe:V, GaAs, InP:Fe were reported as having fast response times at low incident intensities of few tens of mW/cm^2 . The reported value of the electro-optic coefficient of CdTe:V is three times larger than that of GaAs and InP. However, the above materials can not be used in the wavelength range of 600 to 700 nm. [1-3]

The as-grown $\text{CdS}_{0.8}\text{Se}_{0.2}$ crystal has a large crystal size, good optical quality, medium to high resistivity, and a good transparency for wavelengths longer than 600 nm. The ternary system offers the capability that its band-gap can be tailored by adjusting the alloy composition, thus the crystals may be optimized for use at desired wavelengths.

It has been reported that the vanadium dopant is responsible for the high photorefractive gain observed in CdTe:V. Vanadium dopant in CdTe compensates for a high resistivity, and provides additional deep levels. [1] We assume that vanadium dopant in CdSSe would have behave similarly to the vanadium dopant in CdTe.

We present here the first results of photorefractive two-beam coupling measurements on a $\text{CdS}_{0.8}\text{Se}_{0.2}$ single crystal doped with vanadium. The measurements were performed at 633 nm using a 5 mW cw He-Ne laser. We also present the photoluminescence and absorption spectra. These results are discussed and compared to that of vanadium-doped CdTe crystals and a pure CdS crystal reported previously [1-4].

Theory

In a photorefractive two-beam coupling experiment (Fig. 1), two beams of unequal intensity intersect inside the semi-insulating sample to form a spatially sinusoidal interference pattern. In the region of constructive interference the charge carriers are excited to the band states, undergo diffusion, drift, and are recaptured by traps. These effects result in charge redistribution and give rise to the space-charge field. This field, acting through the linear electro-optic effect, modulates the refractive index of the material. If the grating is displaced with respect to the incident optical interference pattern the beam coupling gives rise to energy transfer from one beam to the other. The grating wave-vector depends on the wave-vectors of the incident beams and the angle between the two crossed beams. The value of grating wave-vector is given by

$$k_g = 2k \sin\theta \quad (1)$$

where 2θ is the angle between the two crossed beams.

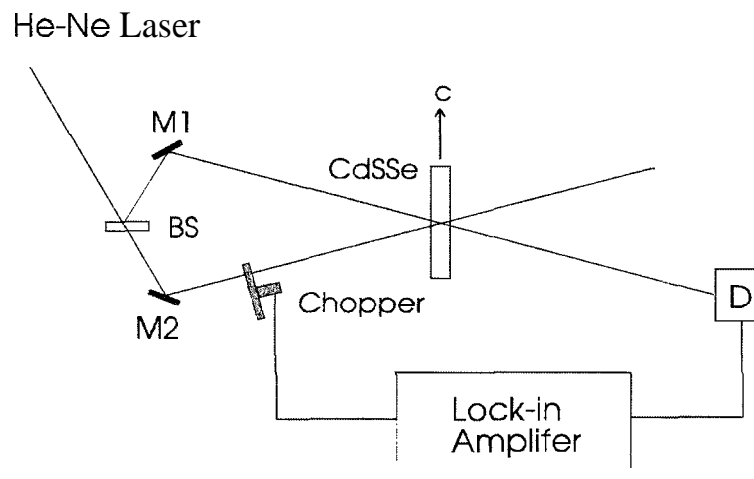


Figure 1: Experimental setup for photorefractive two-beam coupling.

By chopping the pump beam and monitoring the signal beam, the photorefractive gain can be measured. The ratio of the modulation of the signal-beam ΔI_s to the signal beam I_s without pump beam is related to the photorefractive gain Γ . The relation is given by [4]

$$\frac{\Delta I_s}{I_s} = \frac{\exp(\Gamma L) - 1}{1 + \beta \exp(\Gamma L)} \quad (2)$$

where L is the overlap length between two beams and β is the intensity ratio of the signal beam to pump beam.

According to a simplified model given by Kukhtarev and others, the photorefractive gain Γ can be predicted by the formula [1]

$$\Gamma = \frac{2\pi(n_0^3 \gamma_{eff})}{\lambda \cos\theta} \left(\frac{KT}{e}\right) \frac{k_g}{1 + (k_g^2/k_D^2)} \xi \quad (3)$$

where ξ is the electron-hole competition factor, k_D is the inverse of the Debye screening length, and γ_{eff} the effective electro-optic coefficient, For an one level model, $k_D^2 = (e^2/\epsilon KT) N_{eff}$ where N_{eff} is the effective trap density and ϵ is the dielectric constant. The γ_{eff} depends not only on electro-optic properties of the crystal, but also on the sample orientation and beam polarizations, this relation is

$$\gamma_{eff} = \hat{e}_1^* (R k_g) \hat{e}_2 \quad (4)$$

where R (3×3×3) is the linear electro-optic tensor, k_g (3×1) is the unit grating wave-vector, \hat{e}_1^* (1×3) and \hat{e}_2 (3×1) are the unit polarization vectors of signal and pump beams, respectively. CdSSe belongs to the hexagonal 6 mm symmetry group with nonzero electro-optic coefficients, $y_{13} = \gamma_{23}$, γ_{33} (γ_{42}) = γ_{51} . For the experimental configuration used in this study, $\gamma_{eff} = y_{13}$.

Results and Discussion

A single crystal of CdS_{0.8}Se_{0.2}:V was grown by horizontal physical vapor transport (PVT) method along with a concentration of 150 ppm (nominal) vanadium for creating trap center. The starting materials were supplied by Cleveland Crystals, Inc., with a labeled purity of 99.995%. The as-grown crystal had a diameter of 12 mm and a length of 6 cm. A sample from this crystal was cut and polished to a 8×5×4 mm³ rectangular parallelepipeds with the orientation shown in Fig. 1. The resistivity was measured by applying silver-paint contacts on the 3 x 3 mm² area and measuring the I - V curve. The resistivity is in excess of 10⁷ Q-cm at voltages up to 100 V.

The absorption spectra measured at room temperature is shown in Fig. 2. The spectrum shows a absorption edge at 585 nm and a long tail. The absorption edge corresponds to the bandgap of the semiconductor crystal and the absorption tail is assumed to be from the vanadium dopant. An absorption coefficient of 2.3 cm⁻¹ was obtained at 633 nm. This value is comparable to that of a CdTe:V sample with vanadium concentration 5 × 10¹⁶ /cm³ [3].

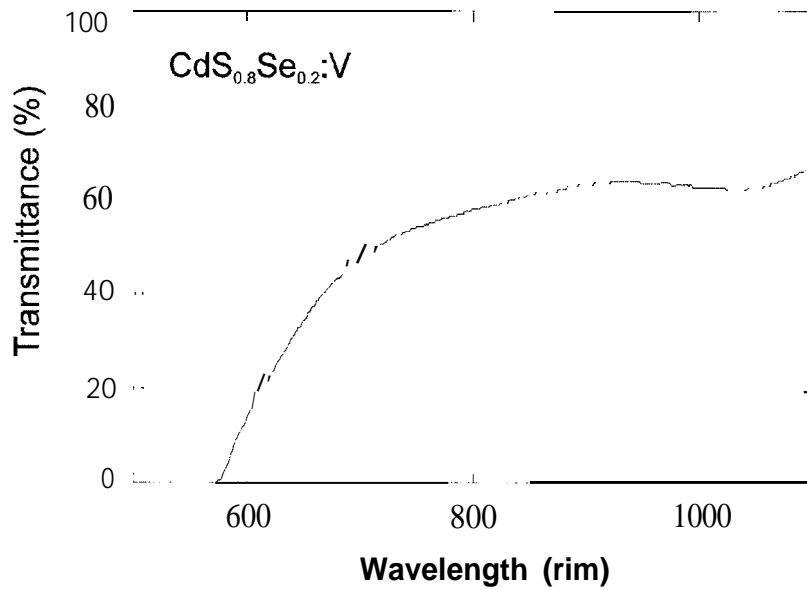


Figure 2: Room temperature absorption spectrum of $\text{CdS}_{0.8}\text{Se}_{0.2}:\text{V}$.

Photoluminescence (PL) measurements were performed at 5.8 K. Fig. 3 shows the PL spectrum of a $\text{CdS}_{0.8}\text{Se}_{0.2}:\text{V}$ crystal. A strong bound exciton peak is located at 2.313 eV with two phonon replicas at 2.279 and 2.244 eV. The spacing of the phonon replicas is about 35 meV, which is between the longitudinal (LO) phonon of 38 meV in CdS and the LO phonon of 24 meV in CdSe [6]. The broad band from 1.7 to 2.1 eV (centered at 1.925 eV) is attributed to a defect center. Similar emission band was observed in a vanadium-doped CdTe, but the exact nature of the centers

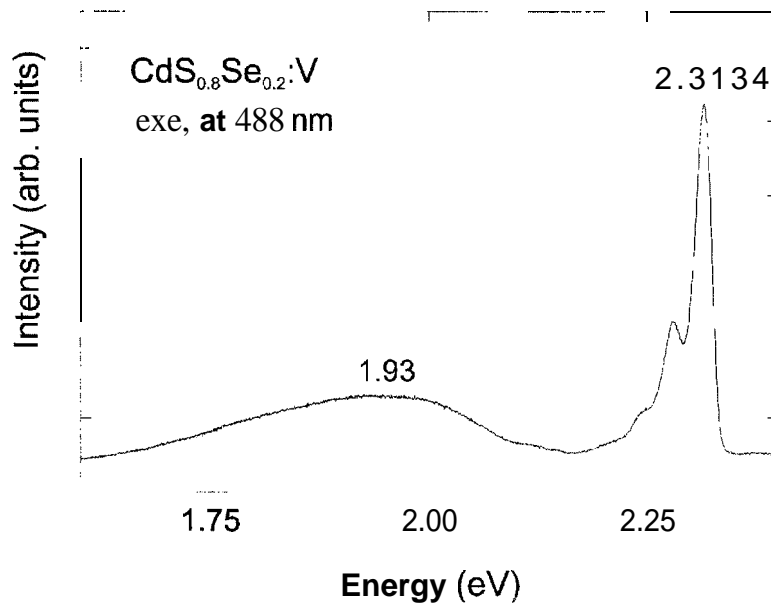


Figure 3: Photoluminescence spectrum at $T = 5.8\text{K}$.

responsible for these emissions is still unknown or is a matter of speculation [5]. It should be noticed that the wavelength of 633 nm (1.959 eV) from the He-Ne laser matches well with this impurity band observed in PL spectrum.

The photorefractive properties were studied by two-beam coupling at 633 nm using a 5 mW cw He-Ne laser. Two s-polarized Gaussian beams (beam size is about 1.2 mm in diameter) with a beam intensity ratio of $\beta = I_s(z=0)/I_p(z=0) = 0.41$ interfered inside the crystal. The grating wave vector was oriented along the c-axis of the crystal. The pump beam was modulated at 84 Hz by a chopper. The beam-coupling gain Γ reached a value of about 0.24 cm^{-1} at a maximum intensity of 60 mW/cm^2 (I_p) and a grating spacing around 1.6 μm . This gain coefficient is similar to the value reported for a CdTe:V sample at 1.32 μm with an intensity of 10 mW/cm^2 [3] and for a pure CdS crystal at 633 nm with an intensity of 80 mW/cm^2 [4]. The value of photorefractive gain decreases significantly with decreasing laser intensity. The Γ value decreased to one fourth for an incident intensity of 30 mW/cm^2 . Our CdS_{0.8}Se_{0.2}:V sample has a relatively lower resistivity ($10^7 \Omega\text{-cm}$) than that of a pure CdS crystal ($10^{10} \Omega\text{-cm}$), a higher photorefractive gain therefore could be expected at a higher laser intensity when the photo excited carrier concentration exceeds the thermally excited carrier concentration. The gain coefficient exhibits a large fluctuation at different points on the sample. This implies some degree of inhomogeneity in our sample. We also performed the two-beam coupling experiment at 800 nm by using a cw Ti:sapphire laser, but no gain signal beyond noise can be obtained. The results we observed are therefore attributed to the resonant enhancement of the photorefractive response due to photo-excitation near the band edge of the crystal.

Conclusion

We have reported the first observation of the photorefractive effect in a CdS_{0.8}Se_{0.2}:V crystal at wavelength 633 nm using a cw He-Ne laser. The observed photorefractive gain is comparable to that of the best photorefractive semiconductors. The CdS_xSe_{1-x}:V crystals maybe fabricated with a large size, a high resistivity, and controllable defect densities. This material therefore has potential as a fast and sensitive photorefractive material in the wavelength range of 600 to 700 nm.

Acknowledgments

This Research is supported by the NSF Grant HRD-9550605, US Air Force Grant GFY1457096-03120, and NASA Grant NAGW-2925.

References

- [1] R. B. Bylisma, P. M. Bridenbaugh, D. H. Olson, and A. M. Glass, "Photorefractive properties of doped cadmium telluride", Appl. Phys. Lett. 51, 889 (1987).
- [2] A. Partovi, J. Millerd, E. M. Garnire, M. Ziari, W. H. Steier, S. B. Trivedi, and M. B. Klein, "Photorefractivity at 1.5 μm in CdTe:V", Appl. Phys. Lett. 57, 846 (1990).

- [3] J.-Y. Moisan, N. Wolffer, O. Moine, P. Gravey, G. Martel, A. Aoudia, E. Repka, Y. Marfaing, and R. Triboulet, "Characterization of photorefractive CdTe:V: high two-wave mixing gain with an optimum low-frequency periodic external electric field", *J. Opt. Soc. Am. B* 11, 1655(1994).
- [4] P. Tayebati, J. Kumar, and S. Scott, "Photorefractive effect at 633 nm in semi-insulating cadmium sulfide", *Appl. Phys. Lett.* 59, 3366 (1991).
- [5] R. N. Schwartz, M. Ziari, and S. Trivedi, "Electron paramagnetic resonance and an optical investigation of photorefractive vanadium-doped CdTe", *Phys. Rev. B* 49, 5274 (1994).
- [6] A. K. Arora and A. K. Ramdas, "Resonance Raman scattering from defects in CdS", *Phys. Rev. B*, 4345 (1987).