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Defect-related optical absorption bands in $CdSiP_2$ crystals

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Abstract: When used as optical parametric oscillators, $CdSiP_2$ crystals generate tunable output in the mid-infrared. Their performance, however, is often limited by unwanted optical absorption bands that overlap the pump wavelengths. A broad defect-related optical absorption band peaking near 800 nm, with a shoulder near 1 μm, can be photoinduced at room temperature in many $CdSiP_2$ crystals. This absorption band is efficiently produced with 633 nm laser light and decays with a lifetime of ~0.5 s after removal of the excitation light. The 800 nm band is accompanied by a less intense absorption band peaking near 1.90 μm. Data from eight $CdSiP_2$ crystals grown at different times show that the singly ionized silicon vacancy (V_{Si}^-) is responsible for the photoinduced absorption bands. Electron paramagnetic resonance (EPR) is used to identify and directly monitor these silicon vacancies.

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1. Introduction

Cadmium silicon diphosphide ($CdSiP_2$, or simply CSP) is a rapidly emerging versatile nonlinear optical material [1-4]. CSP has the advantage of being a nonoxide crystal with a wide transparency range, thus allowing the output of solid-state lasers to be transferred deep into the mid-infrared. Compared to the widely used $ZnGeP_2$ crystals, CSP has a higher nonlinear coefficient (d_{36} = 84.5 pm/V), can be pumped at shorter wavelengths (between 1 and 1.5 μm), and can produce non-critically phasematched output near 6.5 μm [2]. Recently, ultrafast optical parametric sources, using CSP crystals and pumped near 1 μm, have generated high-repetition-rate picosecond and femtosecond pulses at high average powers across the 6-7 μm spectral range [3,5-8]. Improvements in the growth of high quality CSP crystals are continuing [2,9-11], and computational studies are exploring electronic, optical, and mechanical properties [12,13].

Recently, Golden *et al*. [14] used electron paramagnetic resonance (EPR) to show that CSP crystals may contain significant concentrations of native defects. Paramagnetic charge states of three vacancies (silicon, cadmium, and phosphorus) and an antisite (silicon-on-cadmium) were identified. The silicon and cadmium vacancies are acceptors and the phosphorus vacancy and the silicon-on-cadmium antisite are donors. CSP crystals are usually compensated (with nearly equal concentrations of donors and acceptors) and thus have few free carriers at room temperature. Optical absorption bands associated with these donors and acceptors are expected to affect the performance of an optical parametric oscillator (OPO). When one or more absorption bands overlap the pump wavelength, the maximum output power of the OPO will be reduced and thermal lensing will occur.

In the present paper, we describe the optical absorption bands that are photoinduced in CSP crystals at room temperature by 633 nm laser light. A broad band peaking near 800 nm with a shoulder near 1 μm is dominant and is accompanied by a less intense band peaking near 1.90 μm. A study of eight CSP crystals grown at different times shows that the intensities of these photoinduced absorption bands correlate with the intensities of the EPR spectrum assigned to singly ionized silicon vacancies (V_{Si}^{-}) [14,15]. In the as-grown crystals, the majority of the silicon-vacancy acceptors are in their doubly ionized state (V_{Si}^{2-}) and the silicon-on-cadmium antisite donors are also in a doubly ionized state (Si_{Cd}^{2+}). The laser light then moves an electron from an acceptor to a donor and forms paramagnetic V_{Si}^{-} and Si_{Cd}^{+}

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defects. After removing the 633 nm light, the photoinduced absorption bands decay with a lifetime of 0.5 s as electrons are thermally released from Si_{Cd}^{+} antisites and return to V_{Si}^{-} acceptors (i.e., the initial concentrations of V_{Si}^{2-} acceptors and Si_{Cd}^{2+} donors are restored). In some of our CSP samples, small absorption bands and V_{Si}^{-} EPR signals were initially present and then grew during the 633 nm exposure.

2. Experimental details

$CdSiP_2$ crystals are tetragonal (space group $I\bar{4}2d$) and belong to the II-IV-V_2 family of chalcopyrite materials. Reference [14] provides a detailed description of the structure of the $CdSiP_2$ crystals. Undoped single-crystal boules of $CdSiP_2$ were grown at BAE Systems (Nashua, NH) using the horizontal gradient freeze method [9]. Small rectangular samples with approximate dimensions of 3 × 3 × 5 mm^3 were cut from each boule. Growth-run numbers (24, 30, 32, 40, 41, 44, 45, and 46) are used to label the eight samples in our study. EPR spectra were taken with a Bruker spectrometer operating near 9.40 GHz. Optical absorption spectra were obtained with a Cary 5000 spectrophotometer from Varian. Changes in the charge states of acceptors and donors were photoinduced at room temperature with 12 mW of 633 nm light from a cw He-Ne laser. At room temperature, the optical band edge of CSP is near 530 nm.

3. Results

3.1 Photoinduced optical absorption

Figure 1(a) shows the optical absorption spectra from a $CdSiP_2$ crystal (sample 46). These data were obtained at room temperature using unpolarized light propagating along the [100] direction, i.e., the *a* axis of the crystal. A spectrum was taken before exposure to light (lower black curve) and then again during exposure to 633 nm laser light (upper red curve). Figure 1(b) shows the difference spectrum (i.e., "light on" minus "light off"). The photoinduced absorption spectrum in Fig. 1(b) has a primary peak near 800 nm, a shoulder near 1 μm, and a smaller peak near 1.90 μm. Similar results were obtained from the other seven samples in our study. Figure 1 shows these photoinduced absorption spectra from the set of eight samples.

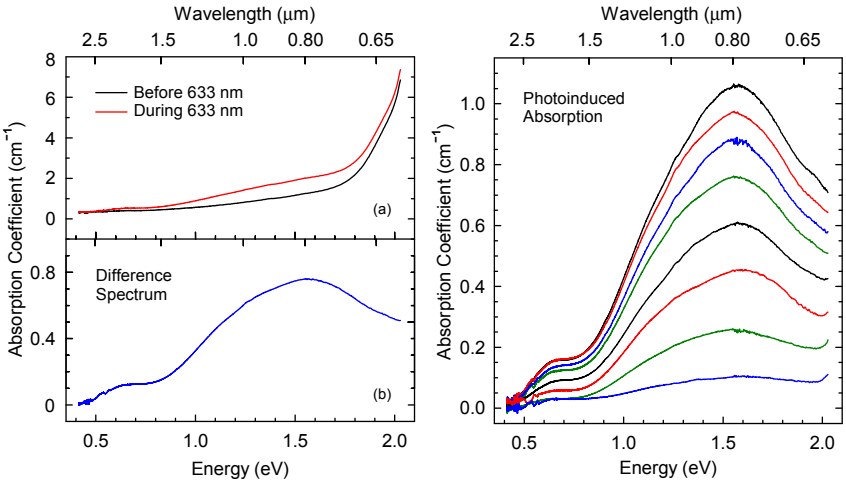


Fig. 1. Optical absorption spectra taken at room temperature from a $CdSiP_2$ crystal. (a) Spectra taken before (lower black curve) and during (upper red curve) exposure to 633 nm laser light. (b) Difference spectrum showing the photoinduced absorption. (Right side) Difference curves for eight $CdSiP_2$ crystals showing the photoinduced absorption produced during illumination with 633 nm laser light. Each curve represents "light-on" minus "light-off". In descending order, these are samples 30, 44, 32, 46, 45, 40, 24, and 41.

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All of the curves in Fig. 1 have nearly the same shape. The intensity ratios of the primary band at 800 nm, the shoulder near 1 μm, and the smaller band at 1.90 μm do not vary among the eight samples. This suggests a common origin for these photoinduced absorption features. Interestingly, these three absorption bands in CSP correspond closely to three bands previously reported in $ZnGeP_2$ crystals [16,17]. Polarization properties were not investigated in the present study. However, an earlier study of an as-grown CSP crystal by Zawilski *et al*. [9] showed that the band at 1.90 μm is only seen with e-polarized light, while the other more intense bands at 800 nm and 1 μm are seen with both e- and o-polarized light.

3.2 Photoinduced silicon-vacancy EPR spectrum

Figure 2 shows the EPR spectra obtained at room temperature from sample 30. Trace (a), taken before exposure to laser light, has a well-resolved set of lines in the magnetic field region from 300 to 370 mT that are due to Mn^{2+} ions occupying Cd^{2+} sites. These inadvertently present Mn^{2+} ions do not change charge state during an illumination (i.e., they are not photoactive) and any associated absorption bands are not easily observed because of weak oscillator strengths. Thus, they are not expected to significantly affect OPO performance. Trace (b) in Fig. 2 was taken during exposure to 633 nm laser light. In addition to the Mn^{2+} lines, additional larger features are now present. The difference spectrum ("light-on" minus "light-off") in trace (c) clearly shows these new photoinduced EPR signals without the interference of the Mn^{2+} lines.

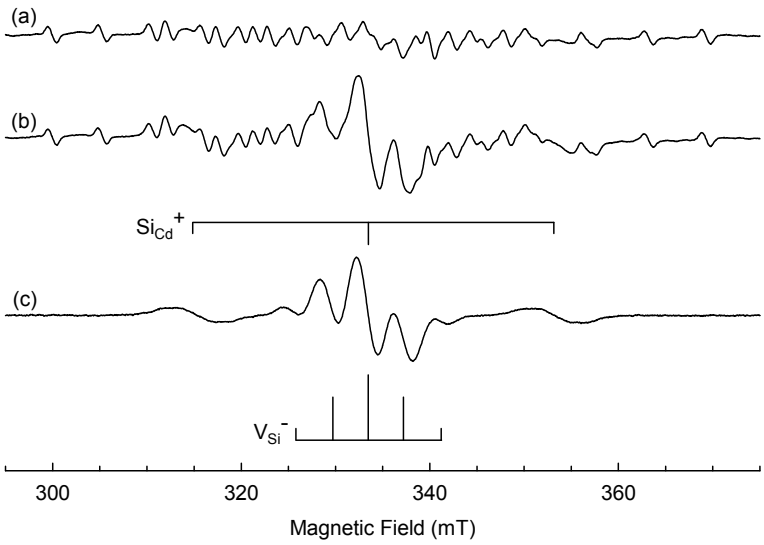


Fig. 2. EPR spectra from a $CdSiP_2$ crystal taken at room temperature with the magnetic field along the *c* axis. (a) Spectrum taken before exposure to 633 nm light. (b) Spectrum taken during exposure to 633 nm laser light. (c) Difference spectrum showing the photoinduced signals from the silicon-vacancy acceptor (V_{Si}^{-}) and the silicon-on-cadmium antisite donor (Si_{Cd}^{+}). Stick diagrams identify the ^{31}P hyperfine lines associated with each defect.

As seen in trace (c) of Fig. 2, the 633 nm light produces a five-line EPR spectrum from singly ionized silicon vacancies (V_{Si}^{-}) and a more widely split three-line spectrum from singly ionized silicon-on-cadmium antisites (Si_{Cd}^{+}). Assignments of these spectra to specific defects were made in earlier EPR studies [14,15,18-20], where analysis of resolved hyperfine interactions with neighboring ^{31}P nuclei provided the key information. In their doubly ionized states, these silicon-vacancy acceptors and silicon-on-cadmium antisite donors are not paramagnetic, and thus are not seen with EPR. Also, no optical absorption bands have been

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associated with the doubly ionized defects. Then, during a 633 nm illumination at room temperature, electrons are temporarily moved from acceptors to donors and paramagnetic V_{Si}^{-} and Si_{Cd}^{+} defects appear along with optical absorption bands. In trace (c) of Fig. 2, the photoinduced concentrations of V_{Si}^{-} acceptors and Si_{Cd}^{+} donors are approximately the same (when the different linewidths are taken into account). These photoinduced EPR spectra in trace (c) of Fig. 2 are present, with varying intensities, in all eight of the CSP samples in our study.

3.3 Correlation of optical absorption and EPR spectra

The EPR spectrum of the silicon vacancy (V_{Si}^{-}) in trace (c) of Fig. 2 and the optical absorption bands in Fig. 1 were photoinduced at room temperature with 633 nm laser light. To explore the possibility of a correlation, data from all eight of our CSP samples were examined. In Fig. 3, the intensities of the photoinduced optical absorption bands in Fig. 1 are plotted versus the intensities of the photoinduced V_{Si}^{-} EPR spectra. Small variations in sample volume and optical path length were taken into account and all measurements were made at room temperature. The data in Fig. 3 show a correlation between the intensity of the photoinduced optical absorption at 800 nm and the concentration of photoinduced singly ionized silicon vacancies. These results suggest that singly ionized silicon vacancies (V_{Si}^{-}) are responsible for the optical absorption bands near 800 nm, 1 μm, and 1.90 μm.

The concentration of singly ionized silicon vacancies in sample 30 was determined to be 1.4×10^{18} cm^{-3} by comparing the intensity of the five-line EPR spectrum to that of the Bruker standard pitch sample. Concentrations of photoinduced V_{Si}^{-} centers for the other seven samples were determined by comparing the intensity of their EPR signals to that of sample 30. Estimates of the uncertainties in the absorption coefficients and EPR concentrations in Fig. 3 are approximately 5%.

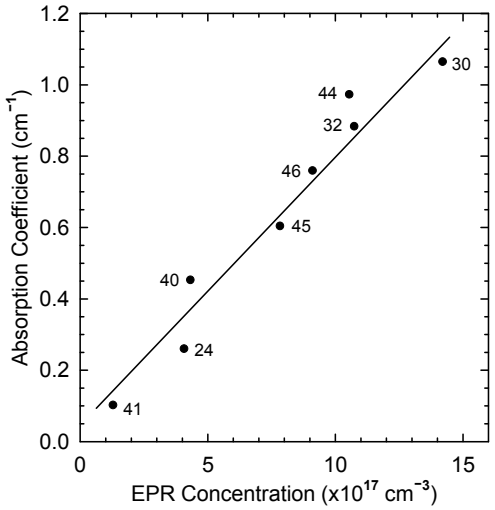


Fig. 3. Correlation of the intensity of the photoinduced optical absorption at 800 nm with the concentration of the photoinduced singly ionized silicon vacancies (V_{Si}^{-}) in the eight $CdSiP_2$ crystals included in this study. The EPR spectra and the optical absorption spectra were taken at room temperature. The solid line is a guide to the eye.

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3.4 Lifetimes of photoinduced optical absorption and EPR signals

Further evidence that the singly ionized silicon vacancies (V_{Si}^{-}) formed during 633 nm illumination are responsible for the photoinduced optical absorption bands in CSP is provided by lifetime measurements. As shown in Fig. 4, the absorption at 800 nm (red line) and the V_{Si}^{-} EPR signal (black line) decay with nearly identical rates at room temperature, after the 633 nm laser light is removed. Data were separately taken in kinetics modes while monitoring the absorption at 800 nm and the peak of the EPR signal from the V_{Si}^{-} acceptor. The characteristic lifetime for the decays of the optical and EPR spectra (i.e., the time for a signal to reach half of its initial intensity) is approximately 0.5 s. These decay curves represent the thermally activated release of electrons from singly ionized silicon-on-cadmium antisites. In Fig. 4, the decay curves are not a single exponential. This suggests that retrapping of the electrons is significant and the decay curves should be described by second-order kinetics.

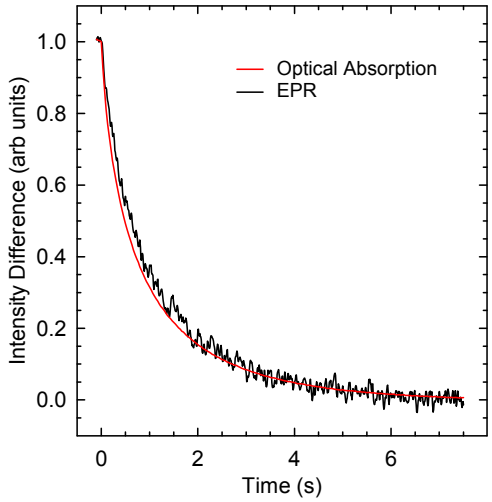


Fig. 4. The decay of the 800 nm optical absorption (red line) and the EPR spectrum from the V_{Si}^{-} silicon vacancies (black line) in a $CdSiP_2$ crystal. The two spectral features were separately monitored after removing the 633 nm laser light. Absorption data are from sample 30 and EPR data are from sample 46.

4. Discussion and summary

In our as-grown CSP crystals, the Fermi level is sufficiently high to allow a majority of the silicon-vacancy acceptors to be in their doubly ionized charge state (V_{Si}^{2-}). At the same time, all of the silicon-on-cadmium antisite donors are in their doubly ionized state (Si_{Cd}^{2+}). The 633 nm laser light then moves electrons from the valence band to antisite donors. Holes generated in the valence band quickly become localized at silicon-vacancy acceptors. The net result is to form significant concentrations of V_{Si}^{-} acceptors and Si_{Cd}^{+} donors during illumination (these charge states thermally decay with the 0.5 s lifetime once the laser light is removed).

The ground state of the singly ionized silicon vacancy is responsible for the three photoinduced absorption bands observed in Fig. 1(b). The 1.90 μm band is assigned to a valence-band-to-acceptor transition with the V_{Si}^{-} center being the participating acceptor (i.e., an electron in the valence band is transferred to the acceptor). In analogy with earlier work in $ZnGeP_2$ [16,17], possible models for the bands in the 800 nm to 1.0 μm region of CSP are (1) an intracenter transition (ground state to a localized excited state of the V_{Si}^{-} acceptor) and (2)

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an acceptor-to-donor transition (an electron moves from the V_{Si}^{-} acceptor to a donor and requires the two defects to be near each other). The intracenter transition could be either the 800 nm or 1.0 μm band, with the acceptor-to-donor transition being the other band.

Although the focus of the present paper is on the photoinduced absorption bands, a broad and small, yet noticeable, absorption in the 0.6 to 2.5 μm region was present in five of our eight CSP samples before exposure to 633 nm light. The shapes of the pre-laser absorptions were not determined precisely, but they appear to be similar to the bands shown in Fig. 1(b). These five samples also had small V_{Si}^{-} EPR signals prior to illumination. The presence of these absorption bands in as-grown samples (before exposure to laser light) can be explained by a slightly lower Fermi level due to either fewer donors or more acceptors. This would result in more silicon vacancies initially being in the singly ionized state rather than the doubly ionized state.

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