

Photoconductive characterization of $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ ($0 \leq x \leq 0.25$) single crystal alloys

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Large grain polycrystalline and single crystals of $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ grown by a modified Bridgman method were studied using the photoluminescence and photoconductivity techniques. The temperature dependence of the band gap, as determined by photoluminescence, follows the Varshni equation for measuring temperature in the range of 15–290 K. One of the fitted parameters, the Debye temperature, monotonically decreases with the increase of the atomic zinc concentration. A close correlation between the photoluminescence and photoconductivity measurements is also found. Samples in which the photoluminescence spectra exhibit emission bands associated to cadmium vacancies and other structural defects, show a photoresponse curve which includes, in addition to the intrinsic band, another broad band at lower energies. Using the ionization energies of the defect related bands in the photoluminescence spectra we have identified the second band in the photoresponse curve due to the photoexcitation of trapped carriers at levels related with the structural defects.

I. INTRODUCTION

In the last few years large area $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ single crystals and thin films have gained a lot of attention.¹⁻³ Much of the interest in this material has developed because of its potential applications to detectors of radiation in the infrared spectral region and to solar cells. Since the band gap of $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ can be tuned throughout the range of 1.5 to 2.25 eV by adjusting the stoichiometry, its application to photovoltaic devices is specially attractive for the fabrication of high efficiency tandem solar cell structures. In addition, many schemes for the fabrication of infrared detectors require epitaxial layers of other ternary alloys such as HgCdTe , for this application high crystalline quality and large diameter CdTe and $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ single crystals are the substrates of choice.

In this paper we report on the photoluminescence properties of polycrystalline and single crystal $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ ($0 \leq x \leq 0.25$) wafers. From the analysis of the photoluminescence (PL) spectra it is found that the single crystals have a high degree of crystalline perfection and that the polycrystalline samples exhibit as the dominant photoluminescence (PL) emission a broad band located in the spectral region generally associated with radiative recombination via structural defects. On the other hand, the photoconductivity (PC) spectra show a qualitative agreement with the model of de Vore for both single crystal samples, the CdTe and the ZnCdTe alloys. For the case of the polycrystalline samples we observe a broad band at the low energy side of the band

edge which frequently has been observed for samples containing either impurities or imperfections. From the analysis of PL we deduce that this band is associated with the crystalline imperfections in the polycrystalline samples. Measurements of the photocurrent as a function of the chopper frequency give an estimation of the recombination lifetimes. We found that for our samples the low and high chopper frequency regimes leads to two different recombination lifetimes.

II. EXPERIMENTAL

For the present study, we have used large grain polycrystalline and single crystals $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ samples grown by a modified Bridgman method at Galtech Semiconductor Materials Corporation. The stoichiometric composition was determined by electron microprobe analysis and from the energy position of the main exciton line observed in the low temperature PL spectra. None of the samples were intentionally doped, and the single crystals had a room temperature resistivity in the range of 5×10^6 to $8 \times 10^8 \Omega \text{ cm}$ for $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ and of approximately $8 \times 10^8 \Omega \text{ cm}$ for the pure CdTe . The resistivity of the polycrystalline mixed material was measured in several individual single crystal grains ($\sim 0.3 \times 0.3 \times 0.3 \text{ mm}^3$) and it was in the range of 5×10^5 to $8 \times 10^6 \Omega \text{ cm}$. For this work the single crystal samples were cleaved along the (110) surface in an Ar atmosphere and the PL measurement was done immediately after the cleaving procedure. In the polycrystalline samples the PL measurement was taken from a fresh, shiny but crystallo-

graphically nonidentified surface also obtained by cleavage. For the PL measurements the crystals were placed in a variable temperature helium gas closed-cycle refrigerator where the temperature can be stabilized within 0.2 K over the range of 11 to 300 K. As the excitation source we used a He-Ne laser focused on the sample using cylindrical optics, the laser power impinging on the sample was of approximately 1 mW. The photoluminescence was measured with a Jobin Yvon double spectrometer with a resolution of about 0.15 meV in the visible range.

Photoconductivity measurements were made at room temperature using a standard Faraday box in series with a Keithley 246 power supply and a PAR model No. 124 A lock-in amplifier with a model No. 184 current preamplifier. Silver paste was employed for the electric contacts. A conventional optics was used to focus the light on the samples. Monochromatic light was obtained from a 250 W halogen tungsten lamp passed through a Jobin Yvon HR 1000-M monochromator. The slits were set at the maximum aperture capable of achieving a resolution of 0.002 at 1.959 eV. Photoresponse measurements were made using a United Detectors PIN photodiode and normalized for a unit light intensity. An SR541 Stanford Research Systems chopper was used

to make measurements of the photoresponse as a function of the chopper frequency allowing us to change the frequency from 10 up to 2500 Hz.

III. EXPERIMENTAL RESULTS

A. Photoconductivity

Figure 1 shows the variation of the band gap with temperature for Zn_xCd_{1-x}Te single crystals with $x = 0$, (a); $x = 0.03$, (b); $x = 0.1$, (c); and $x = 0.25$, (d). The data-points were obtained by adding 0.013 eV to the energy position of the (D^0, X) line in the PL spectra measured at various temperatures in the range of 14 to 280 K. The energy 0.013 eV corresponds to the difference between the (D^0, X) line and the bottom of the conduction band. The continuous line is the best fitting of the experimental points to the Varshni equation⁴:

$$E_g(T) = E_0 - [\alpha T^2 / (\beta + T)]. \quad (1)$$

In Fig. 2 we show typical room temperature photoresponse (PR) curves (photocurrent for unit light intensity) as a function of photon energy in the range of interest for three Zn_xCd_{1-x}Te single crystals with $x = 0, 0.03$, and 0.25 . The three curves follow qualitatively the de Vore's model⁵ which predicts a maximum photocurrent around the band gap energy caused by intrinsic excitation. The exact position of that maximum depends on the particular surface recombination mechanism. The applied voltages were $V = 10, 30$, and 30 V for $x = 0.0, 0.03$, and 0.25 , respectively.

Figure 3 compares the room temperature PR curves for two Zn_xCd_{1-x}Te samples grown from the same source material with a nominal composition of $x = 0.10$. The continuous curve corresponds to a single crystal sample whereas the broken curve to a polycrystalline sample. The spectrum of the polycrystalline sample shows, in addition to the band due to intrinsic excitation, a broad band located 0.15 eV below the band gap energy. Notice that the intrinsic excitation band maximum does not correspond to the position of the band gap energy. All the polycrystalline samples with

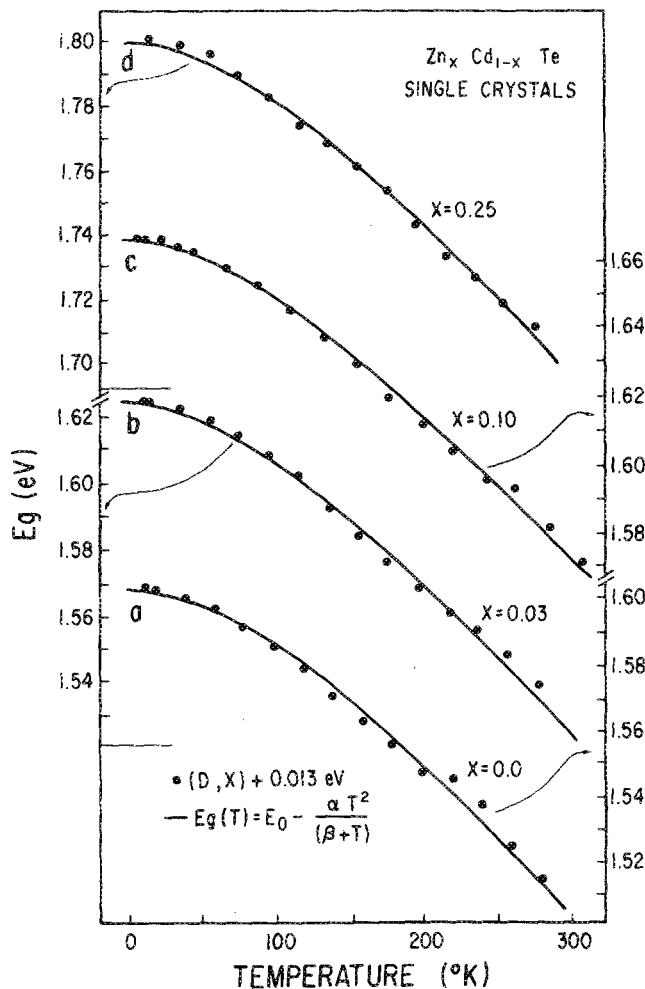


FIG. 1. Plot of the energy-gap values as a function of temperature for Zn_xCd_{1-x}Te single crystals with $x = 0, 0.03, 0.10$, and 0.25 . The data-points were obtained from PL measurements. The full lines correspond to the adjusted Varshni equation with the parameters given in Table II.

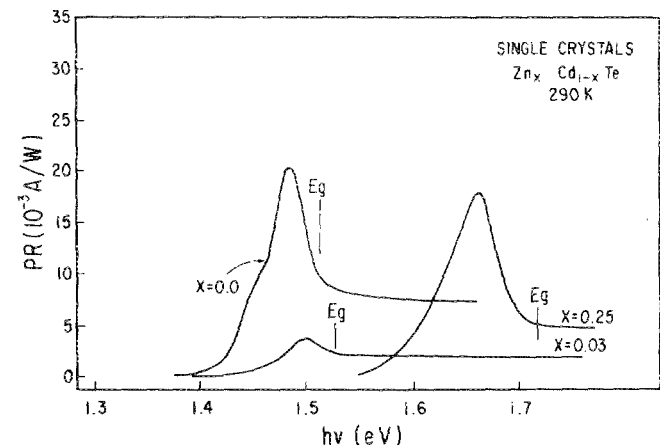


FIG. 2. Room temperature photoresponse vs photon energy for Zn_xCd_{1-x}Te, $x = 0, 0.03$, and 0.25 .

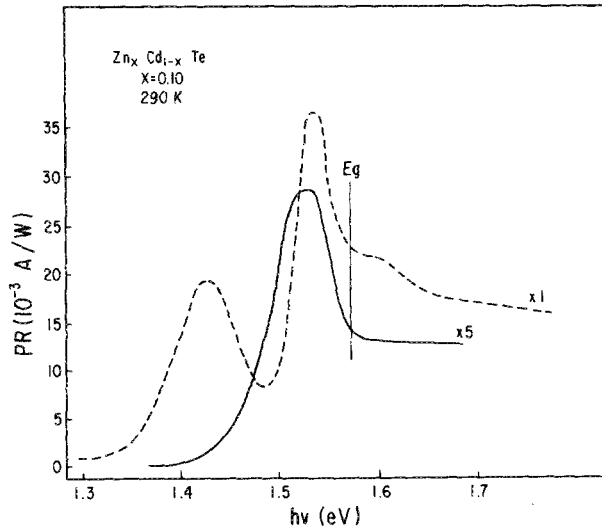


FIG. 3. Room temperature photoresponse curves vs photon energy for Zn_xCd_{1-x}Te with $x = 0.10$, for a single crystal (full line) and for a polycrystalline sample (broken line).

different values of x measured in this study, show this broad band located below the energy gap. All measurements in Figs. 2 and 3 were taken with chopper frequency of 113 Hz.

The dependence of the photoresponse as a function of the reciprocal chopper frequency for a CdTe single crystal is shown in Fig. 4. The continuous curve is the best fitting of equation

$$i = i_{\text{stat}} \tan h(1/4\tau\nu), \quad (2)$$

obtained by Ryvkin⁶ and applied to various semiconductor materials.⁷ In Eq. (2) i_{stat} is the stationary state current (dc current), τ the recombination time of carriers, and ν is the chopper frequency.

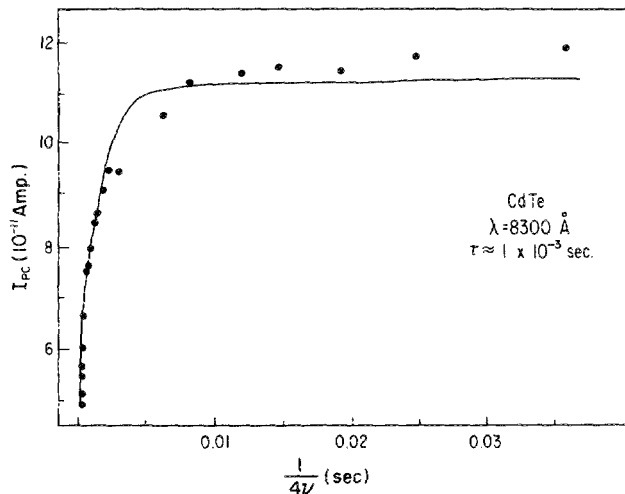


FIG. 4. Room temperature photocurrent vs $1/4\nu$, where ν is the chopper frequency for a CdTe single crystal measured at $\lambda = 8300 \text{ \AA}$.

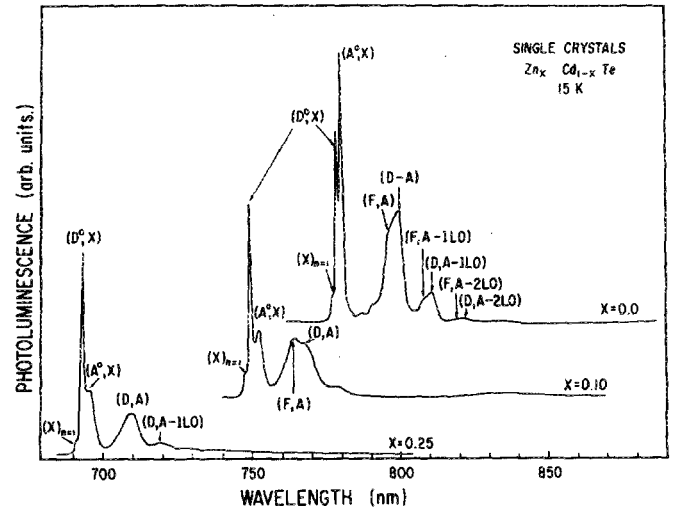


FIG. 5. Low temperature photoluminescence spectra of Zn_xCd_{1-x}Te single crystal cleaved surfaces. Line assignments are given in Table I.

B. Photoluminescence

In Fig. 5 we show a typical 15 K PL spectra for Zn_xCd_{1-x}Te ($x = 0.25$ and $x = 0.10$) and for CdTe ($x = 0$) single crystal cleaved surfaces. All three spectra are plotted with the same abscissae. As can be seen from that figure, the PL spectra is dominated by near-band-edge PL. Lines due to exciton recombination, transitions between free electrons and acceptor levels (F, A) and donor and acceptor levels (D, A) are observed in the PL spectra. Notice that for wavelengths above the (D, A) line, emission due to recombination of pairs from levels associated with structural defects and deeper impurities is basically absent in these single crystal spectra. The notation used in Fig. 5 has been adopted from the literature⁸ and the origin of the various lines deduced from the detailed measurement of the dependence of the spectra on temperature and excitation intensity. Line notation and assignments of CdTe and Zn_xCd_{1-x}Te PL spectra is given in Table I.

Figure 6 shows the 15 K PL spectra for Zn_xCd_{1-x}Te ($x = 0.13$ and $x = 0.1$) polycrystalline cleaved surfaces. In contrast to the single crystals, a broad and intense emission

TABLE I. Notation and positions of the observed lines in the PL spectra of Zn_xCd_{1-x}Te single crystals (Ref. 8).

Notation	Position, nm (eV)		
	$x = 0$	$x = 0.1$	$x = 0.25$
(X) _{n-1}	777.2(1.5955)	748.0(1.6577)	692.0(1.7919)
(D ⁰ , X)	778.3(1.5932)	749.5(1.6544)	693.3(1.7885)
(A ⁰ , X)	779.5(1.5907)
(A ⁰ , X)	...	752.3(1.6483)	695.4(1.7831)
(F, A)	795.5(1.5588)	764.0(1.6230)	709.0(1.7489)
(D, A)	798.0(1.5539)	768.5(1.6135)	...

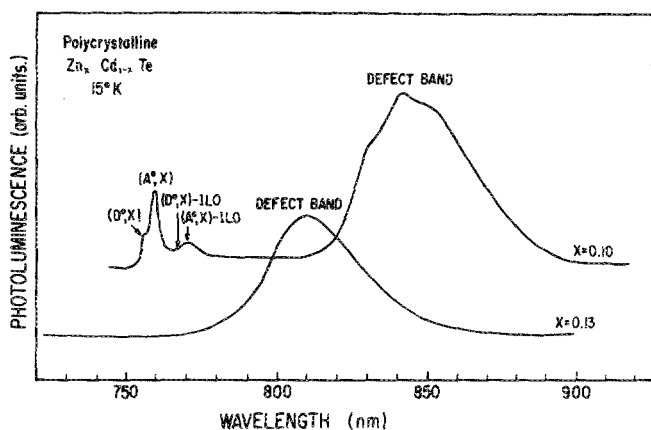


FIG. 6. Low temperature photoluminescence spectra of Zn_xCd_{1-x}Te polycrystalline samples with $x = 0.10$ and 0.13 . Line assignments are given in Table I.

band located at approximately 100 nm above the wavelength corresponding to the band gap dominates the PL spectra of the polycrystalline samples. For the samples with $x = 0.1$ in addition to that broad defect-related band one observes weaker lines at about 760 nm with the recombination of excitons bound to D^0 and A^0 levels. The first phonon replica, 0.022 meV below the main exciton lines, is also observed in the spectrum.

Figure 7 shows the PL spectra in the range of excitonic and donor-acceptor recombination for a Zn_xCd_{1-x}Te ($x = 0.03$) single crystal cleaved surface recorded at various temperatures in the range of 15–280 K. All peaks become broader as the sample temperature increases. The lines relat-

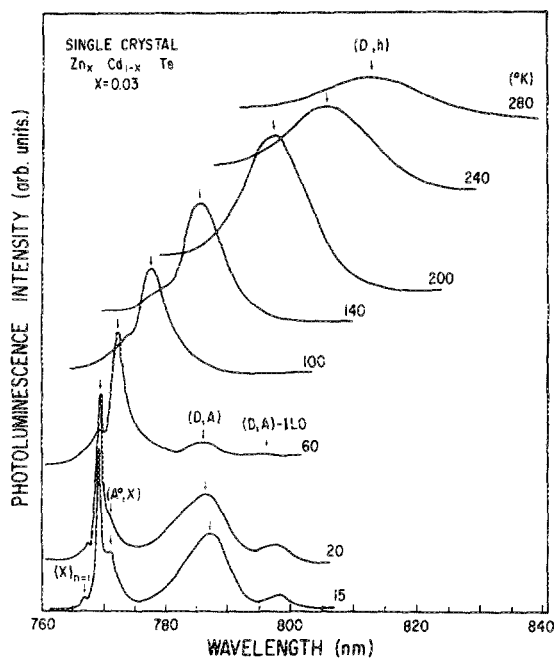


FIG. 7. Temperature dependence of the near-band-edge photoluminescence spectra for a Zn_xCd_{1-x}Te with $x = 0.03$ single crystal.

TABLE II. Parameters of the Varshni equation for the different Zn concentrations in Zn_xCd_{1-x}Te.

X	E_0 (eV)	$\alpha(10^{-4} \text{ eV/K})$	β (K)
0.0	1.605	6.48	285
0.03	1.625	6.48	276
0.10	1.668	6.48	264
0.25	1.800	6.49	265

ed with the recombination of free and bound excitons move to longer wavelengths (lower energies). The fact that the line located at about 769 nm in the 15 K PL spectrum exists at higher temperatures is possibly due to the superposition of a donor-valence band (D, h) recombination with (D^0, X) .⁹ The peak shift is due to the shrinkage of the band gap energy with increasing temperature. Contrary to the excitonic lines, the (D, A) transition moves to shorter wavelengths (higher energies) for temperatures up to approximately 60 K and then vanished for higher temperatures. The latter is the expected temperature behavior for a (D, A) transition.¹⁰ The temperature dependence of the spectra of other Zn_xCd_{1-x}Te single crystals with different composition measured under similar conditions are not shown because they follow the same general trends as in Fig. 7, however, in the polycrystalline samples, the emission band related with structural defects is indistinguishable from the background noise, for temperatures higher than 230 K.

IV. DISCUSSION

As shown in Fig. 1 the $E_g(T)$ values, determined from the PL measurements, follow the Varshni's equation in the measured temperature range. The parameters obtained from the fitting of the equation to the experimental $E_g(T)$ points are collected in Table II. In the second column, the $E_g(T = 0)$ is given for CdTe and for Zn_xCd_{1-x}Te with $x = 0.03, 0.1$, and 0.25 . We found that the α value ($= 6.48 \times 10^{-4} \text{ eV/K}$) is basically independent of x and similar to the one reported for pure CdTe.¹¹ We also found a Debye temperature with a tendency to decrease with the increase of x . For $x = 1$ a Debye temperature of 219.3 K has been reported.¹²

The spectra in Figs. 5 and 6 show that the PL spectra of single crystal samples is dominated by excitonic recombination which indicates a high crystalline perfection. In contrast, the main emission line in polycrystalline samples is a broad band located approximately 0.15 eV below the band gap energy whose origin has been previously associated with structural defects in the illuminated layer. In a recent study, González-Hernández *et al.*¹³ have shown that the incorporation of Zn into the CdTe lattice results in a significant reduction of cadmium vacancies in the structure of the mixed crystal. According to preliminary studies of the annealing behavior under Cd atmosphere of the various lines in the PL spectra of pure CdTe crystals, the bands located at about 0.058 eV below the energy corresponding to band gap and denoted with (D, A) and (F, A) in Figs. 5 and 6, are associated with radiative transitions involving acceptor states related with cadmium vacancies.

In Fig. 2 one sees that the photoresponse curves of the Zn_xCd_{1-x}Te single crystals with $x = 0.03$ and 0.25 exhibit only the band due to intrinsic photoconductivity. For the case of the pure CdTe crystal, in addition, the PR curve shows a shoulder located at the lower energy side of the intrinsic band. Although the exact position of that shoulder is difficult to determine it can be estimated that the energy difference from that feature to that of the band gap is of approximately 0.055 eV. Since this energy is rather close to the energy of 0.058 eV determined from the PL measurements for the ionization energy of the acceptor level related to cadmium vacancies, we conclude that the shoulder observed in the PR curve of pure CdTe is caused by the photoexcitation of carriers from these levels. Notice that the ionization energy of the cadmium vacancies related levels was obtained from the low temperature PL spectra, however, since the free electron to donor level transition is the dominant radiative recombination path at higher temperatures, the ionization energy of this level should be independent of temperature. The fact that the maximum of the intrinsic photoconductivity is located at energies below the energy gap, as measured by PL, indicates that the recombination of carriers at surface states plays a key role even in those cleaved surfaces.¹⁴ The importance of surface preparation on the intrinsic PL band is now under study.

Polycrystalline samples exhibit a PL and PC spectra with features that are not observed in the single crystal spectra. Due to the large grain size in the samples (~ 1 mm²) and because of the illuminated volume was contained within a single grain, we believe that the observations reported here are not related to grain boundaries effects.

The broad band in the room temperature PC spectrum of the polycrystalline sample, located about 0.15 eV below the band gap energy is probably related to the photoexcitation of carriers from levels associated with structural defects in the bulk of the single crystal grains. This assignment is based on the following observations: (i) the broad peak observed in the PL spectra of that sample is located 0.15 eV below the energy corresponding to the band gap. A similar PL band in the spectra of CdTe has been previously related with structural defects; (ii) the ionization energies of most impurities in the II–VI compounds are considerably larger than 0.15 eV,¹⁵ and (iii) if the broad band in the PC of these materials is related with impurity levels one should observe it in both spectra in Fig. 3, because both samples were prepared from the same source material.

The position at room temperature of the defect band which is located at about 845 nm at 15 K in the PL spectra of the polycrystalline sample in Fig. 5, was determined from direct PL measurements as a function of temperature, since this band vanishes for temperatures above 230 K we extrapolate to obtain its position at room temperature.

The recombination lifetime is obtained as a fitting parameter in Eq. (2). As shown in Fig. 4, we were not able to fit the experimental data with a single expression of the type of Eq. (2) in the whole frequency range investigated. A previous analysis of the frequency dependence of the photocurrent in organic semiconductor shows a behavior in which two different recombination lifetimes were necessary to get a good fitting of the experimental points.⁷ In our case, it is found that all measured single crystal samples show basically a different τ for the low- and high-frequency domains, indicating different dynamics for the recombination of carriers in these two regimes. We found that the high-frequency recombination time is about 1 ms for a less-than-gap photon energy and 10 ms for a higher-than-gap photon energy. We are currently trying to establish the correlation of these values with the surfaces and bulk conditions.

V. CONCLUSIONS

We have found a close correlation between the PC and PL spectra of Zn_xCd_{1-x}Te ($0 < x < 0.25$) specially in those samples having structural defects. For this study single crystal and polycrystalline samples were used. The PC spectra of the former show the typical intrinsic band and the PL spectra with only near-band-edge emission lines. However, the polycrystals show, in addition to these features, a broad and intense PL band in the spectral region associated with structural defects and a broad PC band located at energies below the intrinsic feature.

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