

Deep energy levels in CdTe and CdZnTe

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The deep levels present in semiconducting CdTe and semi-insulating CdTe:Cl and Cd_{0.8}Zn_{0.2}Te have been investigated by means of cathodoluminescence, deep level transient spectroscopy (DLTS), photo-induced current transient spectroscopy, and photo-DLTS. The latter two methods, which can be applied to semi-insulating materials, allow to characterize the deep traps located up to midgap and can determine whether they are hole or electron traps. We have identified 12 different traps, some common to all the investigated samples, some peculiar to one of them. A comparison of the results obtained from the various materials is given and the status of defect models is reviewed. © 1998 American Institute of Physics. [S0021-8979(98)02504-3]

I. INTRODUCTION

CdTe and its related compounds are characterized by a relatively large band gap, by a good mobility-lifetime product, and by a high average atomic number. Moreover, it has been shown that they have interesting optical properties in the 1–1.5 μm spectral range.^{1,2} The combination of these features makes CdTe a promising material for applications as γ - and x-ray detectors and as electro-optic devices and in telecommunications. In order to obtain the high resistivity ($\rho > 10^8 \Omega \text{ cm}$) required for such applications, one should either grow stoichiometric impurity-free crystals,³ or dope them with group III or group VII donors for CdTe growth in Te-rich conditions which produce a high concentration of V_{Cd} native acceptors. These donor impurities compensate the native V_{Cd} acceptors by forming complexes, usually called center A,⁴ which lie at approximately $E_v + 0.15 \text{ eV}$.^{5–7} Due to their shallow location in the band gap, the existence of an extra deep trap located near midgap has been hypothesized in order to explain the pinning of the Fermi level observed in semi-insulating materials.^{5,6,8,9} The investigation of deep traps in CdTe and related compounds is thus necessary to understand their electrical and optical properties, in particular whether their high resistivity is achieved by a compensation process.

The aim of this work is to identify and characterize the deep levels present in semiconducting (undoped CdTe) and semi-insulating II–VI compounds (CdTe:Cl and Cd_{0.8}Zn_{0.2}Te). While CdTe:Cl is made semi-insulating by the presence of Cl via a compensation process,^{5,9} Cd_{0.8}Zn_{0.2}Te is intrinsically highly resistive. We have carried out cathodoluminescence (CL) measurements to optically characterize the materials and to have data on electronic levels to compare with those reported in the literature, mostly obtained by optical characterization methods. In order to increase the spectral resolution and to determine whether the level is a hole or

electron trap, we have utilized junction spectroscopy techniques, namely deep level transient spectroscopy (DLTS), photo-induced current transient spectroscopy (PICTS), and photo-DLTS (PDLTS). While DLTS can only be applied to semiconductors, PICTS and PDLTS allow the study of deep traps in semi-insulating materials and, in particular, the traps located near midgap which otherwise are difficult to detect. Finally, a comparison of the results obtained from the various materials analyzed allowed us to advance hypotheses on the origin and character of most of the deep traps.

II. EXPERIMENT

We have investigated four different sets of samples, all p -type: CdTe undoped ($\rho = 30 \Omega \text{ cm}$), CdTe:Cl ($\rho > 10^7 \Omega \text{ cm}$), CdTe:Cl annealed at $T = 600^\circ \text{C}$ in an Ar atmosphere for $t = 5 \text{ h}$, and Cd_{0.8}Zn_{0.2}Te ($\rho > 10^{11} \Omega \text{ cm}$). The CdTe samples have been grown with the traveling heater method (THM) while the Cd_{0.8}Zn_{0.2}Te ones have been grown by the high pressure Bridgman method (HPB). The undoped CdTe material is semiconducting and the CdTe:Cl and the Cd_{0.8}Zn_{0.2}Te samples are semi-insulating. Schottky diodes

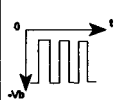
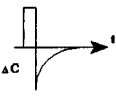
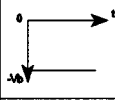
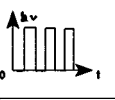
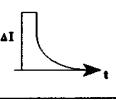
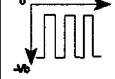
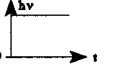
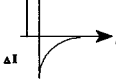
Transient Spectroscopy	Electrical excitation	Optical excitation	Output signal	Carrier traps
DLTS		none		majority
PICTS				majority and minority
P-DLTS				majority

FIG. 1. Spectroscopic modes of investigations applied in this research work.

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TABLE I. Energy and capture cross section of the deep levels found in the investigated samples.

	A ₀	A	A ₁	B	C	D	E	F	G	H	H ₁	I
<i>E</i> (eV)	<i>E_v</i> +0.12	<i>E_v</i> +0.14	<i>E_v</i> +0.15	<i>E_v</i> +0.20	<i>E_v</i> +0.25	<i>E_v</i> +0.32	<i>E_v</i> +0.43	<i>E_v</i> +0.57	<i>E_c</i> -0.64	<i>E_v</i> +0.76	<i>E_c</i> -0.79	<i>E_c</i> -1.10
<i>σ</i> (cm ²)	2×10 ⁻¹⁶	1×10 ⁻¹⁶	4×10 ⁻¹⁷	3×10 ⁻¹⁶	8×10 ⁻¹⁷	8×10 ⁻¹⁶	1×10 ⁻¹⁴	8×10 ⁻¹⁴	2×10 ⁻¹³	6×10 ⁻¹³	4×10 ⁻¹⁴	9×10 ⁻¹¹

have been prepared by depositing an Au or In barrier on one side of the sample while the backside Ohmic contact has been obtained by electroless Au deposition.¹⁰ Similar results have been obtained with both metals. Junction spectroscopy analyses have been carried out with a SULA Technical system. The DLTS method¹¹ has been applied to the semiconducting undoped CdTe samples while PICTS^{12,13} and PDLTS¹⁴ have been utilized to study the semi-insulating CdTe:Cl and Cd_{0.8}Zn_{0.2}Te samples. These last two methods allow the determination of deep trap parameters (activation energy and capture cross section) in semi-insulating (SI) materials with good resolution, even though the data interpretation is more complex than in DLTS.¹⁵ Figure 1 summarizes the spectroscopic modes of investigation used in this research work, together with their peculiar features. PICTS and PDLTS are complementary as PICTS reveals both majority and minority carrier traps without reliably allowing us to distinguish between them, and PDLTS reveals only majority carrier traps.¹⁴ Thus, a direct comparison between PICTS and PDLTS spectra of the same SI sample can provide indication on whether the deep level is a hole or electron trap. The sample heating rate during the spectroscopic measurements was 0.2 K/s and the emission rate varied from 5 to 2×10⁴ s⁻¹. The excitation wavelengths used in PICTS and PDLTS measurements were λ = 670 nm and λ = 880 nm and no major differences were observed in the resulting spectra. The error associated to the activation energy has been calcu-

lated from a Chi-squared fitting procedure to each data set of the Arrhenius plot and resulted to be approximately 5%. CL analyses have been performed in a Hitachi S-2500 scanning electron microscope at a temperature of 80 K with an accelerating voltage of 25 keV. Emission was measured with a North Coast E0-817 germanium detector.

III. RESULTS

The electrical characterization of the deep levels in the four investigated sets of samples revealed the existence of 12 different traps labeled A₀, A, A₁, B, C, D, E, F, G, H, H₁, and I, some common to all materials, some peculiar to one of them. Their activation energy and apparent capture cross section¹⁶ are reported in Table I. The DLTS analysis of semiconducting undoped CdTe produced the spectrum reported in Fig. 2 where four peaks are clearly visible, A, B, E, and H. As reverse bias DLTS reveals only majority carrier traps, these deep levels are hole traps and their activation energy has to be measured from the valence band. The concentrations of the deep traps, calculated taking into account the λ correction factor,¹⁷ are 1×10¹², 4×10¹², 2×10¹², and 8.5×10¹² cm⁻³, respectively, for levels A, B, E, and H. It should be stressed that the trap concentration is not necessarily proportional to the peak height as it is determined taking into account factors such as the free-carrier concentration and the λ transition region, which vary with temperature, especially in compensated materials. The CL spectrum of the same sample is reported in Fig. 3, showing the near band edge emission, the 1.4 eV band, a broad band centered at about 1.1 eV and a peak at about 0.8 eV.¹⁸ The radiative transitions detected by CL analyses may either have the same energy of the DLTS peaks or the value complementary to *E_g* = 1.54 eV, the energy gap of CdTe. In the case of undoped CdTe the CL emission at 0.8 eV directly correlates

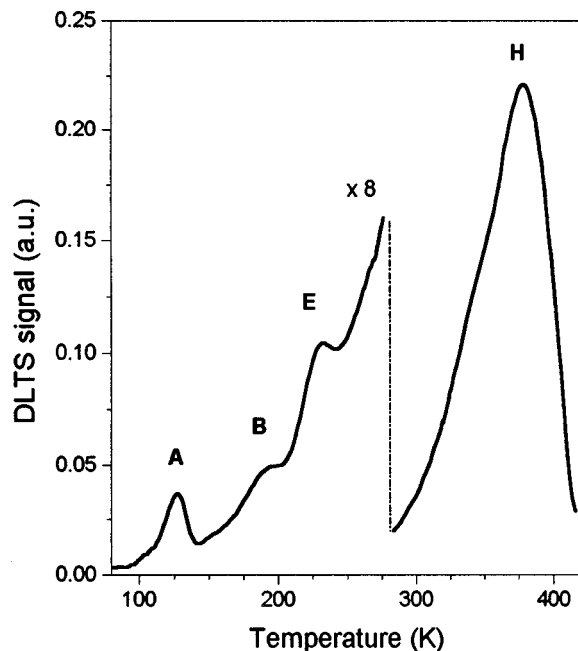


FIG. 2. DLTS spectrum of undoped CdTe. The emission rate is $e_p = 77 \text{ s}^{-1}$, the applied reverse bias is $V_b = -2 \text{ V}$, and the pulse width is $t = 1 \text{ ms}$.

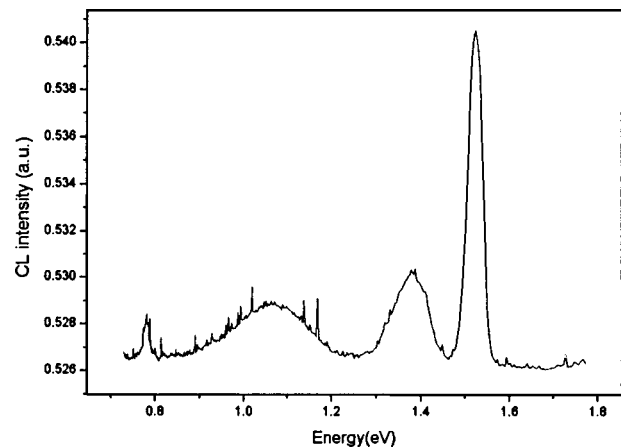


FIG. 3. CL spectrum of undoped CdTe.

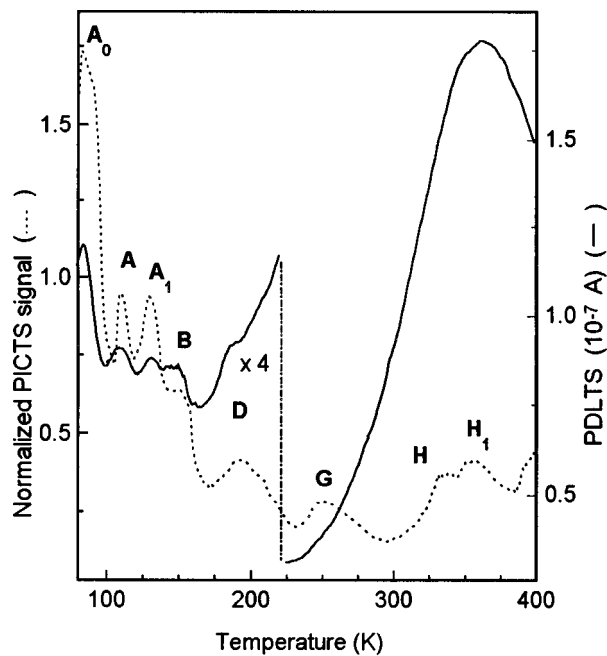


FIG. 4. Comparison of a PICTS (dotted line) and a PDLTS (solid line) spectrum of a CdTe:Cl sample obtained in identical experimental conditions: $V_b = -30$ V and emission rate $e_{n,p} = 370$ s $^{-1}$.

with DLTS level H ($E_v + 0.8$ eV) while the CL band at 1.4 eV is complementary in energy to peak A and the band at 1.1 eV is complementary to peak E ($E_v + 0.43$ eV). The CL spectra of the materials investigated in this research have been described in detail elsewhere^{18,19} and here we will focus our attention on the transient spectroscopy results and on their comparison with the CL ones.

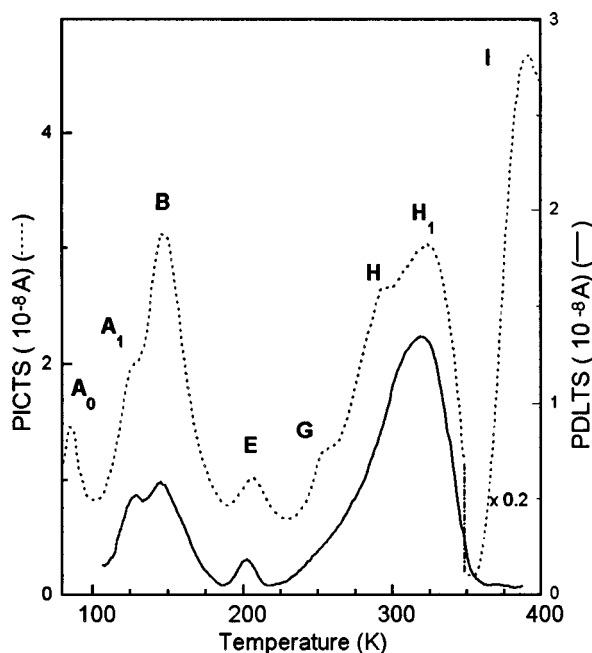


FIG. 5. Comparison of a PICTS (dotted line) and a PDLTS (solid line) spectrum of a CdTe:Cl annealed sample obtained in identical experimental conditions: $V_b = -30$ V and emission rate $e_{n,p} = 77$ s $^{-1}$.

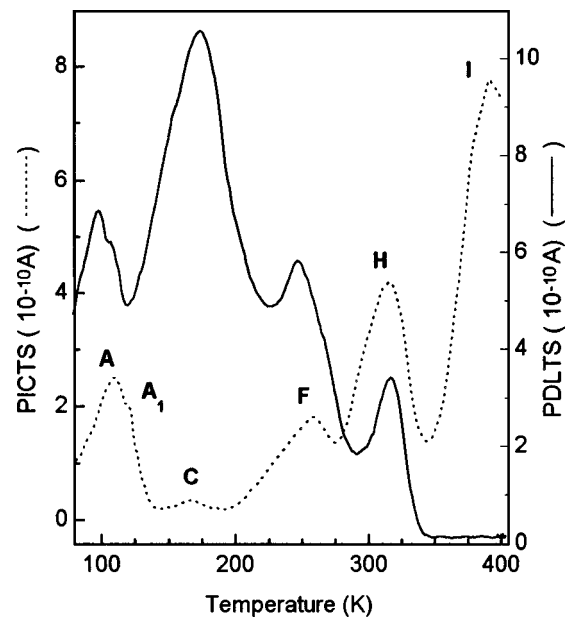


FIG. 6. Comparison of a PICTS (dotted line) and a PDLTS (solid line) spectrum of a Cd_{0.8}Zn_{0.2}Te sample obtained in identical experimental conditions: $V_b = -30$ V and emission rate $e_{n,p} = 370$ s $^{-1}$.

The PICTS and PDLTS analyses on CdTe:Cl revealed the presence of energy levels already detected in undoped CdTe (A, B, H) but new traps are also evident, as shown in Fig. 4. The peaks labeled with the same letter actually correspond to the same trap, as has been verified by comparing the Arrhenius plot of each trap. It is evident that one peak, labeled G, is present in PICTS and disappears in PDLTS. This indicates that it is a minority carrier trap, i.e., an electron trap, and its activation energy has to be measured from the conduction band. After the annealing treatment the PICTS and PDLTS spectra shown in Fig. 5 indicate that the relative heights of the peaks in CdTe:Cl vary: some peaks disappear (A, D) and a new one becomes evident (E). The identification of a trap by simply evaluating the peak position

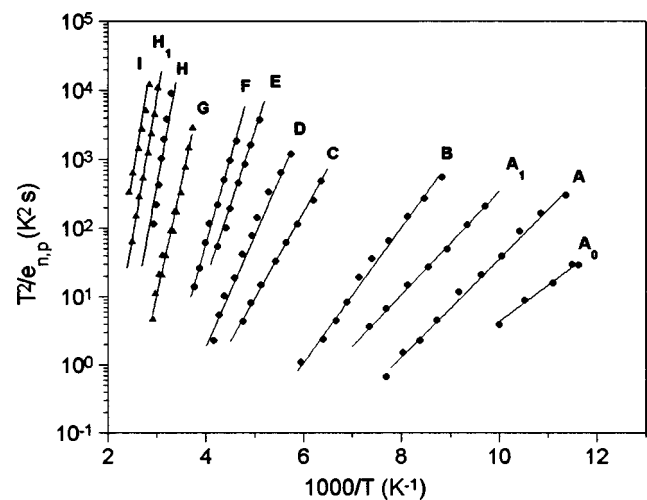


FIG. 7. Arrhenius plots of all the deep levels observed in all the investigated materials by PICTS measurements. The circles represent the experimental data relative to hole traps while the triangles are related to electron traps. The solid lines are the numerical fit of the various data sets.

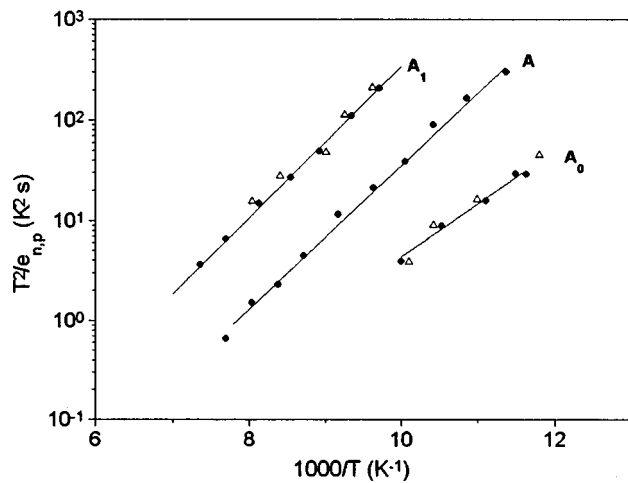


FIG. 8. Arrhenius plots of deep levels A_0 , A , and A_1 observed with PICTS in samples CdTe:Cl before (solid circles) and after (open triangles) the annealing treatment.

as a function of temperature in a spectrum is not significant but it must be done on the basis of an Arrhenius plot. This occurs, for example, in Fig. 5 where peak H_1 in the PDLTS spectrum seems to coincide with peak H of the PICTS spectrum. Level I was already present in CdTe:Cl before the annealing treatment and it is an electron trap because it is present only in PICTS spectra.

The results relative to $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{Te}$ are reported in Fig. 6. Two new levels, peculiar to this material, are present in the spectra, levels C and F , together with traps A , A_1 , H , and I already detected in CdTe samples. All traps, except for level I , are hole traps, i.e., majority carrier traps.

The Arrhenius plots of the identified levels (Fig. 7) have been utilized to calculate the activation energy and the apparent capture cross section of the traps, reported in Table I. As the Arrhenius plot is usually considered the “fingerprint” of each deep level, it has also been used to compare the different traps found in the various materials, as illustrated in Fig. 8. Figure 8 shows, as an example, the Arrhenius plots of levels A_0 , A , and A_1 in samples CdTe:Cl before and after the annealing treatment: it is evident that an identification of the levels present in each sample is quite unambiguous. A com-

parison of the Arrhenius plots obtained with PICTS and PDLTS on the same sample yields similar plots. A summary of all the levels observed is reported in Table II, relative both to the electrical and to the optical characterization techniques. The CL results are often reported as emission bands, as they cannot always be reliably deconvolved into single energy levels.

IV. DISCUSSION

A critical comparison of the results obtained from the four materials investigated results in two different classes of information. By comparing the PICTS and the PDLTS spectra relevant to the same sample it is possible to determine if the level is a hole or an electron trap and, by comparing the Arrhenius plot of the traps, it is possible to attribute an origin and a donor/acceptor character to some deep levels. CL analyses have been extremely useful in comparing our results to those reported in the literature as most of the latter have been obtained with optical characterization methods.

The band gap at room temperature of CdTe ($E_g = 1.54$ eV) is different from the band gap of $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{Te}$ ($E_g = 1.65$ eV),²⁰ and this has to be taken into account when comparing the levels preset in the two materials.¹⁹ A list of the characteristics of deep traps detected in this research work, together with their attribution where available, is reported in the following.

Level A_0 . This level, located at $E_v + 0.12$ eV is only present in CdTe:Cl samples. This strongly suggests its relation to the presence of Cl, in particular to the $(V_{\text{Cd}} - \text{Cl}_{\text{Te}})$ complex, usually called A center.^{5,7} This center plays a significant role in the compensation process of CdTe:Cl as it neutralizes the V_{Cd} native acceptor. Nonetheless, due to its shallow position in the band gap, it cannot be solely responsible for the semi-insulating behavior of CdTe:Cl and another deep trap must intervene in order to pin the Fermi level near midgap (see levels H and H_1).^{5,8,9}

TABLE II. Deep levels found in the investigated samples.

	$\text{Cd}_{0.8}\text{Zn}_{0.2}\text{Te}$			CdTe		CdTe:Cl			CdTe:Cl annealed		
	PICTS	P-DLTS	CL	DLTS	CL	PICTS	P-DLTS	CL	PICTS	P-DLTS	CL
A_0						Yes	Yes		Yes	Yes	
A	Yes	Yes	Yes	Yes	Yes		Yes	Yes	Yes		Yes
A_1	Yes	Yes	Yes		Yes	Yes	Yes	Yes	Yes	Yes	Yes
B				Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
C	Yes	Yes	Yes		Yes			Yes			Yes
D											
E				Yes		Yes	Yes		Yes	Yes	
F	Yes	Yes									
G						Yes			Yes		
H	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
H_1						Yes		Yes			Yes
I	Yes		Yes		Yes	Yes		Yes	Yes		Yes

Levels A and A₁. Level A, with an activation energy of $E_v + 0.14$ eV, has been observed in all materials except CdTe:Cl after the annealing, while level A₁, $E_v + 0.15$ eV, is present in all samples except undoped CdTe. There is no clear attribution for these two levels, which have also been observed in photoluminescence investigations of CdZnTe,²¹ but it has been suggested that they are related to complexes involving a V_{Cd} and a V_{Te} , respectively. Other possible attributions relate them to residual impurities, such as Li or Cu, which may form complexes which differ from the chlorine A center but emit in the same energy range.^{6,22}

Level B. The hole trap located at $E_v + 0.20$ eV is present only in all CdTe samples. As they all may differ in the impurity content and thermal history, it can be related to either of these two factors. The growth process could be a good candidate for the origin of this trap, as it has been reported that different growth techniques influence the formation of defects lying close to the $E_v + 0.15$ eV defect band.²³ Moreover, the Arrhenius plot of our level B coincides with one of the levels found in this energy range for THM grown material.²³ As all CdTe samples are grown with THM while Cd_{0.8}Zn_{0.2}Te is grown with the HPB method, it seems plausible to assign the origin of this level to the THM growth process.

Level C. This level at $E_v + 0.25$ eV is only found in Cd_{0.8}Zn_{0.2}Te samples. A similar level is reported in the literature in Cd_{1-x}Zn_xTe:In at 0.27 eV (Ref. 24) or in Cd_{0.9}Zn_{0.1}Te at 0.31 eV (Ref. 25) and assigned to a Zn related defect, as supported by our results.

Level D. The hole trap located at $E_v + 0.32$ eV is only present in CdTe:Cl before the annealing process. The defects with an activation energy between 0.27–0.35 eV have been attributed in the past to Cu contamination.^{6,26} Another suggested attribution involves a Te_{Cd} complex possibly introduced during the growth process.²⁷ This hypothesis could be supported by our findings as level D is not present in Cd_{0.8}Zn_{0.2}Te (different growth method). Its absence in undoped CdTe could be due to the dominant nearby lying level E, that may mask any effect due to level D. The disappearance of this trap in CdTe:Cl annealed samples could be interpreted as a transformation of the Te_{Cd} defect into V_{Cd} and Te_i , an effect supported by the significant concentration of level E (attributed to V_{Cd} , see below) in the annealed samples.

Level E. The level at $E_v + 0.40$ eV is present in CdTe undoped and in CdTe:Cl annealed samples. It has been previously found in CdTe and attributed to the isolated V_{Cd} .^{25,26} Cadmium vacancies are not easily revealed in CdTe:Cl as they tend to form the center A complex with a Cl donor, leaving the concentration of isolated V_{Cd} very low.²⁸ On the contrary, in CdTe undoped crystals which are not compensated, the V_{Cd} is present in significant concentration.²⁸ In CdTe:Cl annealed samples, both the annealing treatment and the transformation of the Te_{Cd} defect (level D) may account for the appearance of a relevant cadmium vacancy concentration.

Level F. The deep trap located at $E_v + 0.57$ eV is only present in Cd_{0.8}Zn_{0.2}Te and cannot be related to any of the major traps found in CdTe. A trap with a similar activation

energy has been found in PICTS measurements of Cd_{0.9}Zn_{0.1}Te,²⁵ but the Arrhenius plots of these two traps do not have much in common. No emission band associated with this energy has been clearly observed in CL analyses. However, it has been suggested²⁹ that the defect located at 0.55–0.65 eV has an acceptor character and is related to a cation vacancy.

Level G. The trap at $E_C - 0.64$ eV has only been found in CdTe:Cl both before and after the thermal treatment. As it is only present in PICTS spectra, it is an electron trap which, therefore, cannot be revealed and studied in undoped CdTe where only DLTS measurements can be carried out. DLTS measurements on *n*-type CdTe³⁰ reveal the presence of a $E_C - 0.66$ eV electron trap which has been attributed to Cd_i^{++} , possibly associated with an extrinsic impurity. Other results also attribute a trap similar to level G to Cd_i^{++} .^{25,26} Our findings are in agreement with these hypotheses: DLTS and PDLTS measurements, carried out on CdTe undoped and CdTe:Cl respectively, only show hole traps and, thus, level G cannot be revealed.

Level H. The level at $E_v + 0.76$ eV is present in all investigated samples. This deep trap has been reported in the literature studied both with electrical^{19,25,26,30,31} and optical techniques^{7,32} and has been widely attributed to an acceptor complex involving the native V_{Cd} defect and an impurity.^{9,26,28,32} Its thermal emission rates have been measured both for electrons and holes³¹ and resulted to have comparable values. This indicates that the trap behaves as a recombination center and justifies the presence of this level in DLTS spectra of *n*-type CdTe, which only reveals electron traps.^{30,31} This level is located at midgap and intervenes in the Fermi level pinning process which takes place in semi-insulating materials (CdTe:Cl and Cd_{0.8}Zn_{0.2}Te). In semiconducting samples, such as undoped CdTe, it simply acts as a deep center as it is far from the Fermi level.³³

Level H₁. The deep electron trap at $E_C - 0.79$ eV is only present in PICTS spectra of CdTe:Cl, both before and after the thermal treatment, and this strongly suggests its relation with Cl. The presence of Cl induces the formation of the chlorine A center (see level A₀) which compensates the native acceptor V_{Cd} even if it is too shallow to account for the pinning of the Fermi level near midgap. The presence of a further deep donor level located near midgap has been hypothesized in the past^{6,8,9} to fully understand the electrical properties of CdTe:Cl, but to our knowledge such a deep level had not been, so far, experimentally identified.³³ By comparing the data relative to level H₁ in all investigated samples, level H₁ is the only midgap level peculiar to compensated semi-insulating CdTe:Cl. As, moreover, it is present in a high concentration comparable to the recombination center H, it seems plausible to consider it a good candidate for the above mentioned deep donor.

Level I. The $E_C - 1.1$ eV level is present in the PICTS and CL spectra of all samples. The 1.1 eV trap has been found in the past with optical characterization methods in CdTe and Cd_{1-x}Zn_xTe and has been attributed to V_{Te}^{+} .^{6,21,34} This defect is supposed to behave as an electron trap⁴ and, in fact, the trap is not present in the majority carrier spectra (DLTS, PDLTS) of our samples which are all *p*-type.

Energy levels in Cd-based compounds

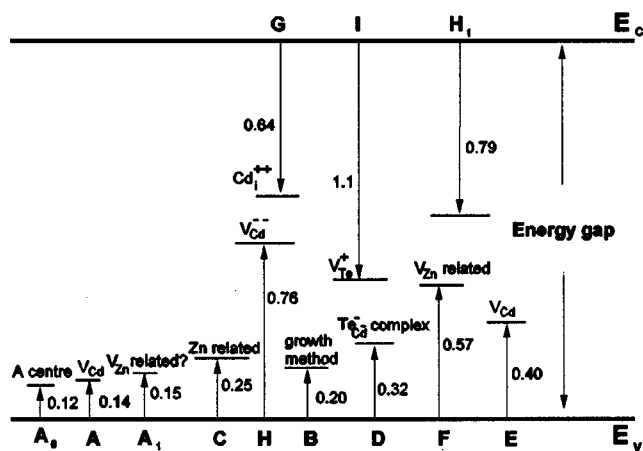


FIG. 9. Summary of the position in the band gap of all the traps observed in the various materials investigated. The trap attribution, where available, is also reported.

Figure 9 summarizes the position in the band gap of the detected deep levels together, where possible, with the trap attribution.

V. CONCLUSIONS

The combined application of complementary spectroscopic techniques, such as DLTS, PICTS, PDLTS, and CL, has allowed the identification of 12 different deep traps in semiconducting and semi-insulating CdTe and $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{Te}$. The hole/electron trap character of these deep levels has been inferred by comparing PICTS and PDLTS spectra, while a critical comparison of the results obtained from the various materials investigated suggested possible attribution of the origin of most defects. In some cases the donor/acceptor nature of the deep traps has also been determined. The analysis of semi-insulating II–VI compounds shed some light on the role played by the defects involved in the compensation process, namely A center and the deep traps located near mid-gap.

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