

Study of the edge and exciton emission in CdTe:Cu:Cl powder samples

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During the last few years several investigations and discussions have appeared concerning the interpretation of radiative electron–hole recombinations in CdTe single crystals. At the same time there is a clear scarcity of experimental information concerning the radiative recombination centres in powder samples of CdTe. Recent progress in CdTe-based thin film solar cells has increased the interest in multicrystalline forms of CdTe, because this material is used as a starting material in many low-cost technologies for producing CdTe thin films. Accordingly, characterization criteria for CdTe powder samples are needed.

Because of high defect concentration in powdered materials it is usually difficult to observe the luminescence in edge-emission and near the band gap regions. The ratio I_d/I_b , where I_d is the intensity of the deep centre defect band (1.42 eV band) and I_b is the intensity of the bound exciton or edge emission line, is often used as a merit parameter for the crystalline quality of CdTe [1]. In good quality crystals and polycrystalline thin films this quantity has a value 0.01 or less. In powder samples this ratio always has a value much higher than 1. In this case the dominating spectral feature is the defect band, and the near band edge features have very low intensity and may often almost completely disappear.

In this letter we report results which, we believe, give some guidelines for the interpretation of photoluminescence (PL) measurements of CdTe powder samples. In this work CdTe powders doped with copper ($N_{Cu} = 1.75 \times 10^{18} \text{ cm}^{-3}$) and chlorine ($N_{Cl} = 6.3 \times 10^{16} \text{ cm}^{-3}$); heat treated under partial vapour pressure of cadmium ($p_{Cd} = 1621 \text{ Pa}$) and quenched from 1073 K were used.

For the PL measurements, a 10 mW Ar-ion laser beam with a wavelength of 488 nm was used for excitation. The laser light was chopped at 277 Hz. The samples were mounted in a closed cycle He cryostat capable of cooling to 12 K. A computer-controlled SPEX 1870 (0.5 m) grating monochromator with spectral slit 0.5 nm was used. The chopped signal was detected with a R-632 photomultiplier using the conventional lock-in technique. The emission spectra were corrected for grating efficiency variations and for the spectral response of the photomultiplier.

A typical luminescence spectrum of powdered CdTe:Cu:Cl at 12 K is presented in Fig. 1. Various observed emission peaks in the spectrum of Fig. 1

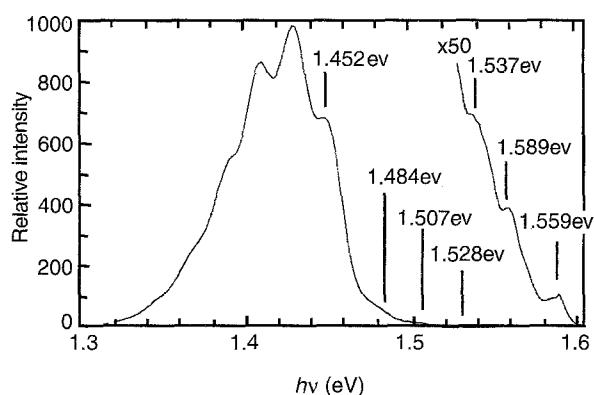


Figure 1 A typical photoluminescence spectrum of the CdTe:Cu:Cl powder samples at $T = 12.4 \text{ K}$.

can be divided into three groups: (i) 1.589, 1.559 and 1.537 eV peaks; (ii) 1.528 eV peak with two LO phonon replicas; and (iii) 1.452 eV band with resolved LO phonon structure. The present letter is concerned with the significance and the interpretation of the weak features (i) and (ii).

The 1.589 eV peak is usually connected with a neutral acceptor-bound exciton line (A^0, X) [2–5]. The excitonic nature of this peak can be verified by studying the dependence of the peak intensity on excitation intensity. A superlinear dependence of I on laser power is indicative of bound excitonic transitions [6]. In our samples a dependence $I \sim I_{\text{laser}}^\alpha$ with $\alpha = 1.31$ was detected, see Fig. 2.

We measured also the temperature dependence of the 1.589 eV peak position, see Fig. 3. The temperature dependence of the peak energy position was

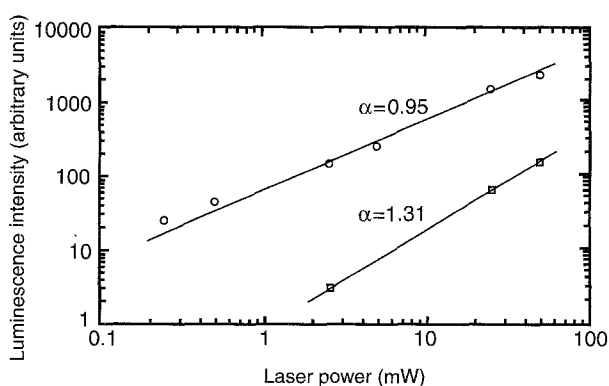


Figure 2 Luminescence intensity dependence on laser power: \circ 1.42 eV band; \square exciton emission.

fitted to the functional relationship for the temperature-dependent energy gap of semiconductors, introduced by O'Donnell and Chen [7]:

$$E(T) = E_g(0) - E_{ex} - S\langle\hbar\omega\rangle[\coth(\langle\hbar\omega\rangle/2kT) - 1] \quad (1)$$

Here $E_g(0)$ is the band gap at zero temperature, E_{ex} is the bound exciton binding energy, $\langle\hbar\omega\rangle$ is the average phonon energy, and S is a dimensionless coupling constant. Taking $E_g(0) = 1.606$ eV [8] a good fit is obtained with the following values: $E_{ex} = 17.5$ meV, $\langle\hbar\omega\rangle = 16.9$ meV and $S = 2.62$. At higher temperatures these parameters result in a value -4.5×10^{-4} eV/K for the temperature dependence dE_g/dT of the energy gap. According to Halsted and Aven [9] the ratio of the dissociation energy (E_{ex}) of the exciton-impurity complex to the ionization energy (E_i) of the impurity is around 0.1 for the excitons bound to acceptor levels. In our case with $E_{ex} = 17.5$ meV we get $E_i = 0.175$ eV. This value is close to the Cu acceptor ground state energy 0.146 eV reported in [10].

The temperature dependence of the bound exciton peak intensity I_{ex} is shown in Fig. 4. As can be seen from Fig. 4, the temperature quenching of the emission intensity proceeds via two different quenching stages. This kind of dependence is possible if there exist two independent luminescence emissions having nearly the same peak-positions. To account for this, the experimental intensity determinations were fitted with the equation

$$I_{ex}(T) = I_{01}/[1 + \alpha_1 \exp(-E_1/kT)] + I_{02}/[1 + \alpha_2 \exp(-E_2/kT)] \quad (2)$$

Here I_{01} , I_{02} are peak intensities at 0 K; E_1 , E_2 are the thermal quenching activation energies for each of the two emission peaks. The following values for the fitting parameters were obtained:

$$I_{01} \approx 127, I_{02} = 80, \alpha_1 \approx 1.3 \times 10^8,$$

$$\alpha_2 = 72.6, E_1 \approx 40 \text{ meV}, E_2 = 17.7 \text{ meV}.$$

The intensities of the components I_1 and I_2 in Equation 2 are equal at 23 K. The first stage of quenching $I_1(T)$ at low temperatures (see Fig. 4) is characterized by an activation energy $E_1 \approx 40$ meV. At higher temperatures the fitted quenching activation energy is $E_2 = 17.7$ meV. The latter value coincides with the exciton binding energy $E_{ex} = 17.5$ meV obtained above through Equation 1. Unfortunately, the small number of experimental points at the low temperature region did not permit us to obtain very accurate values for the quenching process parameters, but it is interesting and obvious that $\alpha_1 \gg \alpha_2$. This very large disparity (1.3×10^8 for α_1 and 72.6 for α_2) cannot be by chance only and certainly deserves further exploration.

Further, we find that the low temperature quenching process of $I_1(T)$ is accompanied by the simultaneous quenching of the 1.559 eV band and its LO phonon replica at 1.537 eV. Therefore we may

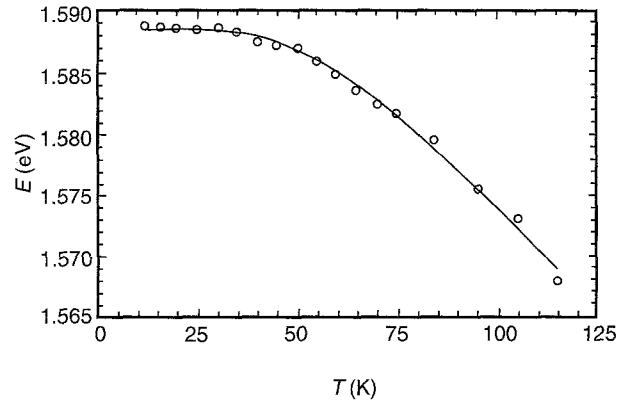


Figure 3 Temperature dependence of the bound exciton peak energy position: \circ measured; — theory.

conclude that the exciton at low temperatures is bound to the same acceptor that is involved in the 1.559 eV band emission. The same conclusion was made in [11]. The simultaneous thermal quenching of the bands is therefore interpreted as the ionization of this acceptor level.

The peak position of the 1.559 eV band did not show any j-shift and therefore we believe that the 1.559 eV band is due to an electron transition from the conduction band to the acceptor level. The depth of this acceptor level can be found using the peak-position of the zero-phonon band and the band-gap value: $E_A \approx 1.606 - 1.559 = 47$ meV. This value does not differ too much from the value 40 meV obtained from the temperature quenching measurements.

Considering the small number of experimental points, this good agreement is probably fortuitous only. The acceptor level $E_A = 50$ meV is commonly assigned to the neutral V_{Cd} [8, 12]. Thus it seems that low temperature $T < 30$ K exciton emission mainly originates from excitons bound to the neutral cadmium vacancy. At higher temperatures the emission from excitons bound to the neutral Cu_{Cd} dominates. The 1.559 eV band itself is due to the free-to-bound transition and is connected with V_{Cd} .

At the edge emission region the weak 1.528 eV PL band with two LO-phonon replicas can be found.

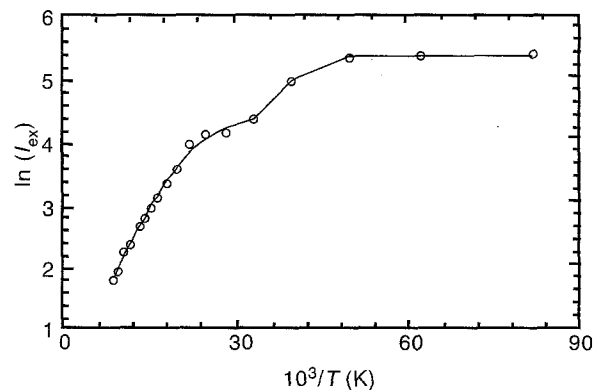


Figure 4 Dependence of the bound exciton peak intensity with inverse temperature in CdTe:Cu:Cl. \circ , experimental; —, theory.

According to [12] this band is due to DA-recombination with $E_D = 15$ meV and $E_A = 67$ meV. The DA pairs model was also proposed in [13]. However, it does not seem to be possible to make a firm assignment of this emission, since in [6] quite a strange behaviour of the 1.528 eV band was observed. In undoped p-type CdTe crystals, after firing in excess Cd pressure, the zero-phonon peak at 1.528 eV reduced significantly in intensity, but at the same time the intensity of its phonon replicas increased. Such behaviour is difficult to explain with a single-band model. A second, experimental, problem is connected with the fact that the self-absorption region of the 1.452 eV PL band, with $E = 1.452 + n\hbar\omega_{LO}$, lies at the same spectral region as the 1.528 eV PL band. Therefore the observation of "true" PL spectra in this energy region may be difficult. In order to clarify this point, further experiments with samples showing a weaker 1.452 eV PL band than our present samples would be needed.

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