

# Cathodoluminescence study of CdTe crystals doped with Bi and Bi:Yb

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**Abstract** Bi doped and Bi and Yb codoped CdTe crystals grown by the Bridgman method have been characterized by cathodoluminescence (CL) in the scanning electron microscope. CL images show a dense network of highly decorated grain boundaries in the Bi doped samples and dopant striations in the codoped crystals, attributed to the presence of Yb. Bi contributes to the appearance of the A luminescence band at 1.43 eV. The influence of Yb dopant on the CL spectra is discussed.

## Introduction

Doping of CdTe crystals with high-Z elements constitutes a very promising way to obtain semi-insulating and photosensitive material suitable for a number of important applications such as room temperature gamma radiation detectors, and infrared optics and optoelectronics [1, 2]. In the particular case of CdTe crystals doped with Bi, we have recently demonstrated that these crystals of reasonably good structural quality could be grown from the melt (Bridgman technique), and vapor (Markov technique) and they have high resistivity and

photoconductivity at the dopant concentrations close to  $10^{17}$  at.cm<sup>-3</sup> [3, 4]. It is also worth mentioning that the Bi dopant could play an important role in a catalytically driven growth of CdTe nanocrystals and nanowires [5, 6].

Two defect centers associated with Bi as dopant have been identified in CdTe crystals by photoluminescence and photoconductivity measurements [7]. The first one is associated with a deep level located at  $E_v + 0.71$  eV, and it is only present at low Bi concentrations and it has a complex structure, donor character, and hole-trap properties. It is responsible for the high resistivity and very good photoconductivity of the CdTe:Bi crystals. The second one is an acceptor center located at  $E_v + 0.30$  eV, assigned to BiTe specie, and is mainly present at high Bi concentrations and is responsible for the low resistivity and poor photoconductivity of highly doped CdTe:Bi crystals.

Besides energetic location of the Bi-related defects, their spatial distribution all over the crystal volume as well as their interaction with other structural defects could be essential for the applications of CdTe:Bi crystals. In our previous studies, we have demonstrated that a complementary use of cathodoluminescence (CL) spectroscopy and imaging is a powerful tool to investigate such problems in CdTe doped crystals (for example, see [8] and [9]). In the present paper, we report the results of CL studies of CdTe crystals doped with Bi. Taking into account an increasing interest in the doping of semiconductor compound crystals with rare-earth elements (for example, see [10]), several CdTe crystals codoped with Bi and Yb were also prepared and investigated.

## Experiment

CdTe:Bi and CdTe:Bi:Yb crystals were grown by the Vertical Bridgman Method in a quartz ampoule with a

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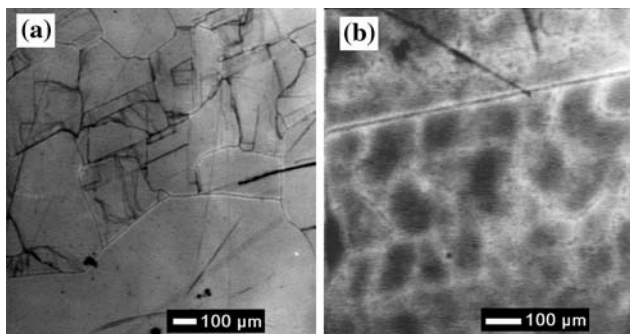
pyrolytic graphite coating, at a growth rate of 0.4 mm/h and a gradient temperature in the solidification zone of 5 °C/cm. The CdTe:Bi crystals were doped with the two Bi concentrations  $1 \times 10^{17}$  at.cm<sup>-3</sup> and  $7 \times 10^{17}$  at.cm<sup>-3</sup> and the respective concentrations of dopants in CdTe:Bi:Yb crystals were  $1 \times 10^{17}$  at.cm<sup>-3</sup> and  $1 \times 10^{18}$  at.cm<sup>-3</sup>. More details on the growth setup could be found elsewhere [4].

CL measurements, spectra and images, were carried out in a Leica 440 SEM and a Hitachi 2500 SEM at 78 K. The CL measurements were carried out at liquid nitrogen temperature by using a R5509 Hamamatsu photomultiplier tube at 20 kV of electron beam energy.

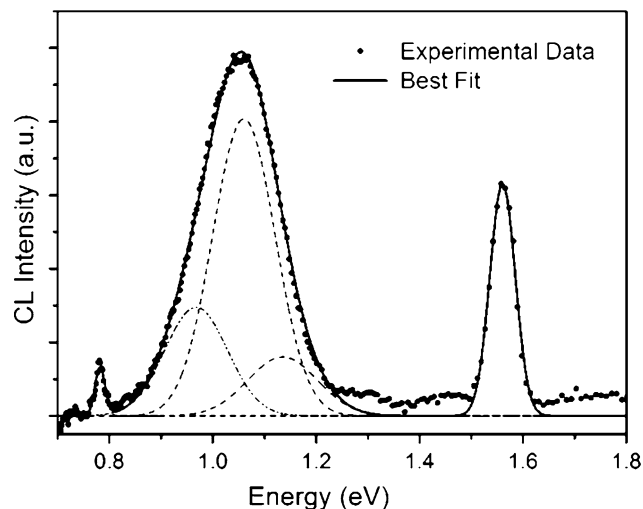
## Results and discussion

Figure 1a shows a CL image of the sample doped with  $1 \times 10^{17}$  at.cm<sup>-3</sup> Bi. Grain boundaries appear as dark lines sometimes surrounded by bright bands at both sides. This contrast, which has been often reported in CL studies of semiconductors and insulator materials, is due to the decoration of the boundaries by impurities and/or point defects. The image shows that the interior of the grains is very homogeneous and no precipitates or other non-radiative recombination centers are observed. By increasing the Bi concentration, sample 2, there is a loss of homogeneity with the formation of a higher number of grains or subgrains with boundaries in which the bright bands extend up to about 50 μm at both sides of the boundary (Fig. 1b).

The CL spectrum of sample 1 (Fig. 2) shows the near band gap emission band at 1.56 eV and two deep level bands centered at about 1.1 eV and 0.781 eV, respectively. Gaussian deconvolution of the most intense band centered at 1.1 eV shows that it has three components at 1.12 eV, 1.06 eV, and 0.96 eV, respectively. The first one can be associated to a level at about 1.1 eV below the conduction band of CdTe, which has been reported in CL and photo-induced current transient spectroscopy studies [11] and it



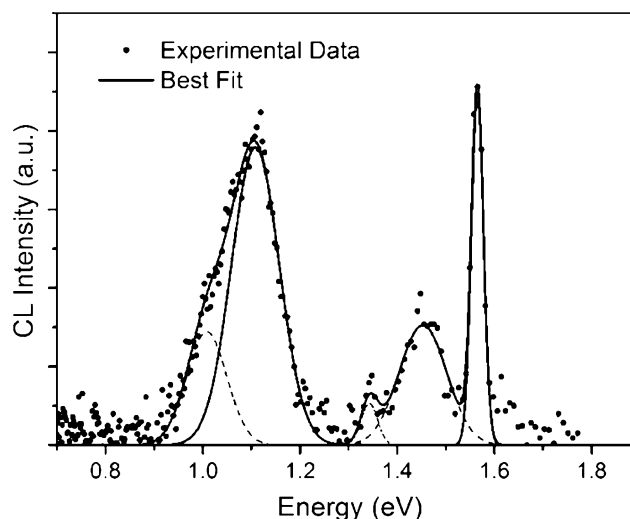
**Fig. 1** (a) CL image of the sample doped with  $1 \times 10^{17}$  at.cm<sup>-3</sup> Bi (b) CL image of the sample doped with  $7 \times 10^{17}$  at.cm<sup>-3</sup> Bi



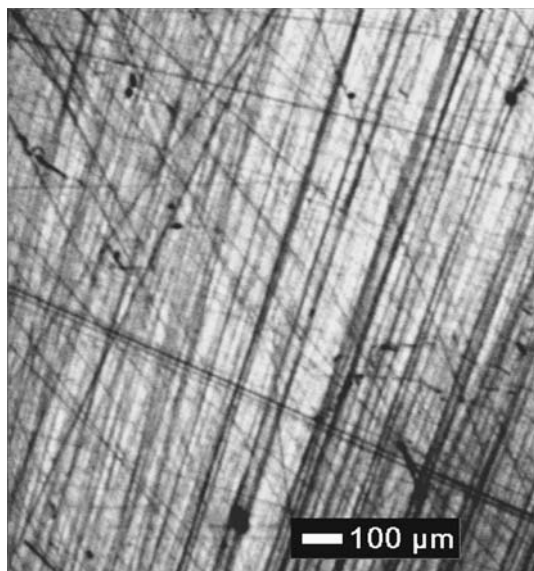
**Fig. 2** CL spectrum of sample 1 at 78 K. Gaussian deconvolution of the band centered at 1.1 eV shows this is a complex band. (Full circles) Experimental data, (solid line) Best Fit, and (dash line) Gaussian components

has been previously suggested to be connected with tellurium vacancies [12, 13]. The other two components are related to cation vacancies and they have an acceptor character [11]. The low energy band at 0.781 eV is also complex, with components at 0.784 eV and 0.775 eV, which are related to different states of an acceptor complex involving the native  $V_{Cd}$  defects and impurities.

Figure 3 shows the CL spectrum of sample 2 with bands at about 1.45 eV and 1.34 eV, in addition to the near band gap emission at 1.56 eV and the deep level band at 1.1 eV, which were also present in sample 1. Comparison of spectra of samples 1 and 2 suggests that the bands at



**Fig. 3** CL spectrum of sample 2 at 77 K. (Full circles) Experimental data, (solid line) Best Fit and (dash line) Gaussian components

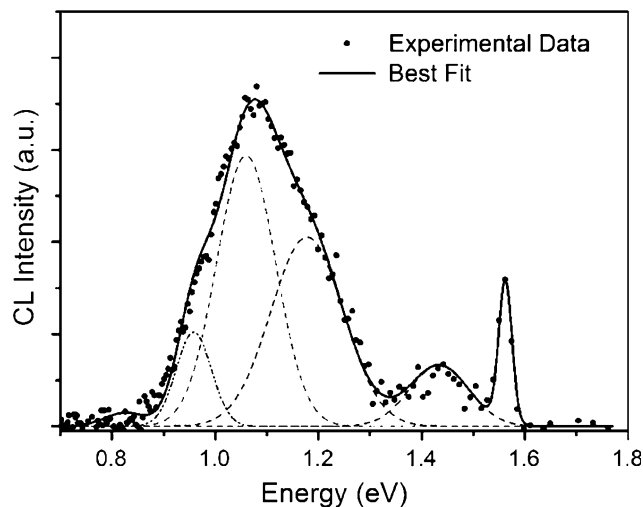


**Fig. 4** CL image of the sample codoped with B and Yb

1.45 eV and 1.35 eV are related to the dopant. In fact luminescence emissions around 1.4 eV in CdTe have been previously reported in doped and undoped material and have been attributed to  $V_{\text{Cd}}$ -donor pairs, called A centers [14, 15]. In this case the 1.45 eV and 1.35 eV bands would be due to A centers formed by cadmium vacancies and bismuth atoms.

The main features observed in the CL images of sample 3, codoped with Bi and Yb, are parallel dark lines as shown in Fig. 4. Such distribution of lines has been reported for other semiconductors [16, 17] and is due to dopant concentration variations. In order to determine which dopant gives rise to the striations, EDX maps for Bi and Yb were recorded but no spatial variations of these elements were detected. We suggest that the concentration of the element is below the detection limit of the EDX although has a strong influence on the dopant sensitive CL measurements.

The CL spectrum of the codoped sample (Fig. 5) shows the band gap emission, a band at about 1.43 eV (band A) and the low energy band centered at about 1.1 eV also found in the Bi doped samples. The A band was not observed in sample 1, which has the same Bi content as this sample, which indicates as the presence of Yb also contributes to this emission. A new radiative center involving Yb atoms is suggested. The influence of Yb is also apparent in the 1.1 eV which is broader than in the other samples and show a slight shift to higher energies showing a maximum at 1.08 eV. Deconvolution of this band shows three components at 1.17 eV, 1.05 eV, and 0.95 eV, respectively.



**Fig. 5** CL spectrum of sample 3, codoped with Bi and Yb. Gaussian deconvolution of the band centered at 1.1eV shows this band is formed by three emission peaks. (Full circles) Experimental data, (solid line) Best Fit, and (dash line) Gaussian components

## Conclusions

Bi doped CdTe crystals with two Bi concentrations as well as crystals codoped with Bi and Yb have been grown by Bridgman technique. CL measurements show that in the sample with higher Bi content ( $7 \times 10^{17} \text{ at.cm}^{-3}$ ) a dense network of highly decorated grain boundaries is formed. In the codoped samples, dopant striations are observed which are probably due to the presence of Yb. Bi doping contributes to the appearance of the A luminescence band. Yb causes a blue shift of the deep level band centered at about 1.1 eV.

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