Material Inhomogeneities in Cd$_{1-x}$Zn$_x$Te and Their Effects on Large Volume Gamma-Ray Detectors

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Abstract
Cadmium zinc telluride (Cd$_{1-x}$Zn$_x$Te or CZT) has shown great promise as a material for room-temperature x-ray and gamma-ray detectors. In particular, polycrystalline material grown by the High Pressure Bridgman method with nominal Zn fraction (x) from 0.1 to 0.2 has been used to fabricate high resolution gamma-ray spectrometers with resolution approaching that of cooled high-purity Ge. For increased sensitivity, large areas (> 1 cm$^2$) are required, and for good sensitivity to high energy gamma photons, thick detectors (on the order of 1 cm) are required. Thus there has been a push for the development of CZT detectors with a volume greater than 1 cm$^3$. However, nonuniformities in the material over this scale degrade the performance of the detectors. Variations in the zinc fraction, and thus the bandgap, and changes in the impurity distributions, both of which arise from the selective segregation of elements during crystal growth, result in spectral distortions. In this work several materials characterization techniques were combined with detector evaluations to determine the materials properties limiting detector performance. Materials measurements were performed on detectors found to have differing performance. Measurements conducted include infrared transmission (IR), particle induced x-ray emission (PIXE), photoluminescence (PL), and triaxial x-ray diffraction (TAXRD). To varying degrees, these measurements reveal that "poor-performance" detectors exhibit higher nonuniformities than "spectrometer-grade" detectors. This is reasonable, as regions of CZT material with different properties will give different localized spectral responses, which combine to result in a degraded spectrum for the total device.
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Introduction

Cadmium zinc telluride (Cd$_{1-x}$Zn$_x$Te or CZT) has been developed for use in room-temperature x-ray and gamma-ray detectors only since 1992 [1,2]. During the few years of development since, however, there has been tremendous improvement such that polycrystalline material grown by the High Pressure Bridgman (HPB) method with nominal Zn fraction ($x$) from 0.1 to 0.2 has been used to fabricate high resolution gamma-ray spectrometers with resolution approaching that of cooled high-purity Ge. In many applications the available radiation level is low, requiring as high a sensitivity as possible. This means both a need for large active areas of more than 1 cm$^2$, and for the detection of higher energy gamma photons, an active thickness on the order of 1 cm or greater. Thus there has been a push for the development of CZT detectors with a volume greater than 1 cm$^3$. So far, detectors as large as 1.5 cm x 1.5 cm x 1.5 cm have been fabricated and evaluated [3,4].

However, nonuniformities in the material at this scale degrade the performance of the detectors. For example, variations in the zinc fraction (and thus the bandgap), and changes in the impurity distributions, both of which arise from the selective segregation of elements during crystal growth, result in spectral distortions. This is particularly a problem in the dimension of a detector in the crystal growth direction. In addition, there is an inherent problem with the poor carrier transport properties of holes as compared to those of electrons. The location of interaction of a gamma event within the detector affects the distances traveled by the electron and hole in reaching the positive and negative electrodes, and thus the pulse response measured. Finally, there are variations in the materials in directions perpendicular to the growth axis because of growth variations.

In this work several materials characterization techniques were combined with detector characterizations to determine the materials properties limiting detector performance. Given the relative effect of composition on bandgap, a one percentage point change in zinc fraction (e.g., from $x=0.095$ to $x=0.105$) results in a change in the energy required to produce an electron-hole pair ($E_{\text{pair}}$) of one-half percent, which means that the amount of charge created, and thus the pulse height measured, changes by 1/2 % across the detector. This leads to a broadening of the
photopeak and a loss in resolution. Thus the inhomogeneity in the zinc composition in a CZT detector leads to a degradation of the spectral response. In addition, in thicker detectors there is also a problem with incomplete charge collection, as the drift length for holes can be less than the distance from the point of photon interaction to the negative contact. This gives rise to "hole-tailing" wherein the low energy side of the photopeak has a long decay down to background. Fig. 1 shows a $^{137}$Cs spectrum from a 1 cm$^3$ CZT detector exhibiting hole-tailing. By mapping out the zinc composition and electrically-active defects, one can determine how large a detector crystal can be "mined" out of a boule without leading to an excessive loss of spectral resolution. There are signal processing approaches being pursued to improve the performance of current large volume CZT spectrometers in the near term by compensating for the poor hole collection problems electronically [5].

**Materials Characterizations**

**Samples Studied**

For the materials characterizations two nominal Cd$_{0.9}$Zn$_{0.1}$Te 1 cm x 1 cm x 0.2 cm detectors from eV Products were used. After detector characterizations the gold contacts were removed to allow for the various materials measurements. One detector, the "spectrometer-grade" device, had good spectral response, while the other, the "poor-performance" device, had little spectral resolution, acting only as a counter.

**Infrared Transmission Microscopy**

A relatively quick and simple qualitative measurement of CZT material quality is infrared transmission microscopy. While the CZT itself is transparent to the IR, precipitates and inclusions like metallic tellurium or cadmium, and other imperfections are opaque to the IR and show up as dark spots. For the work here, a simple IR emitting LED was shone on one side of the samples and the transmitted light collected with lenses and detected with a simple CCD camera with its IR filter removed. Fig. 2a shows the images obtained for both the spectrometer-grade and poor-performance materials. These are negative images, meaning that darker regions indicate higher
transmission. As mentioned above, IR generally highlights the metallic inclusions and precipitates in CZT. The spectrometer-grade material appears to be more uniform than the poor-performance, in that the dark regions are found in uniformly distributed small dots, as opposed to the larger clumps seen in the poor-performance sample. In addition, the spectrometer grade material exhibits diagonal lines of high transmission regions.

One concern in these types of measurements is the presence of surface irregularities, as these will strongly affect the transmission. These samples were polished initially, although it is unclear how the subsequent removal of the contacts affected the surface. However, by focusing through the sample with the collection lens system, it was found that the structure exhibited in the images shown here was in the bulk of the material.

The interpretation of these results is not yet complete. However, some explanations can be attempted. It may be that the predominant mechanism here is the effects of compositional variations. As the zinc fraction, x, increases in CZT the bandgap increases, from 1.44 eV for x=0, or CdTe, to 2.26 eV for x=1, or ZnTe. Regions of higher zinc, and thus larger bandgap, will be more transmitting to the broadband IR from the LED.

**Particle Induced X-ray Emission (PIXE)**

Particle (or proton) induced x-ray emission is a useful technique for probing the elemental composition of the near surface region of samples. In PIXE a focused ion beam is used to excite the elements in a sample, and the characteristic x-rays emitted during relaxation are measured. In this work, 3 MeV protons from a 10 MV tandem accelerator provided the excitation. These protons have a range on the order of 50 μm in the CZT. The x-rays of interest have half-thicknesses on the order of 10 μm, which sets the depth of material probed. A Si(Li) detector was used to characterize the x-ray emissions. Figure 2b shows the PIXE results next to their corresponding IR images. The darkness of a pixel indicates the ratio of Zn to Cd and Te fluorescence x-rays detected, and thus a darker pixel indicates a higher local amount of Zn. As can be seen in the figure, the spectrometer-grade sample exhibits more uniformity than the poor-performance detector. Although the system was not calibrated to determine the absolute
composition, the relative changes in composition across the region were computed. There was a
+/-20% variation about the mean for the spectrometer-grade detector versus a +/-30% variation in
the poor-performance sample. Consistent with the IR results, the PIXE maps show smaller
clumps of higher zinc concentration for the spectrometer-grade sample, and larger clumps for the
poor-performance sample, along with a left-to-right gradation. Further qualitative information is
not apparent.

**Photoluminescence (PL)**

Photoluminescence (PL) is a useful tool for analyzing semiconductor materials. In
photoluminescence the radiative recombination processes are viewed via optical excitation. In this
work the excitation source was the 488 nm line of an argon ion laser. The luminescence was
detected with a double-pass spectrometer coupled to a photomultiplier tube. Two sets of
experiments were conducted. In the first set the samples were cooled in a liquid helium cryostat to
around 4.2 K and the excitation not focused to give the low temperature PL response averaged
over a large portion of the crystal. In the second set of experiments, the sample was held at room
temperature on a precision translation stage and the beam focused to about 3 μm to give a detailed
map of the room temperature PL.

Several peaks are visible in the near band-edge PL spectrum for CZT samples including free
excitons, donor-bound excitons, and acceptor-bound excitons [6,7]. Fig. 3 shows a small region
of the PL spectra near the bandgap from the spectrometer-grade and poor-performance detectors.
A strong neutral-donor-bound exciton (D0-X) peak and a weaker neutral-acceptor-bound exciton
(A0-X) peak are evident. The D0-X peak is much narrower in the spectrometer-grade sample than
the poor-performance sample, and other features can be resolved. In terms of photon energy, the
widths of the D0-X peaks, ΔE/E₀, are 1.8 x 10⁻³ and 3.3 x 10⁻³ respectively. In general, the
sharpness of the peaks in PL spectra relates to the "quality" of the crystal. Variations in the crystal
structure, electrically-active impurity distributions, or other properties lead to broadening of the
features. A particularly effective mode in CZT would be the composition variations. Since the Zn
fraction (x) has a significant effect on the bandgap, changes in x result in shifts in the PL spectrum.
When looking at the integrated PL spectrum from a large area, these shifted responses combine to give the broadened features measured.

There have been several attempts to relate a measured material property with the exact zinc fraction, $x$. From PL it is possible to measure the bandgap to a high precision and accuracy and to detect small changes in the bandgap to the meV level. The difficulty has been in relating the bandgap to the zinc composition. There are several different fits reported by various researchers. As many factors affect the relation, it is difficult to determine which is universally "correct", as the fit depends on many properties of the particular material being studied. By correlating the PL measurements with the x-ray diffraction work discussed later in this paper, a fit that best represents the material studied here has been developed. Reference 6 discusses this fitting process in more detail.

Given the large uncertainty in the absolute value of the zinc composition, but the high precision in determining relative changes in $x$, the variation in $x$ is more meaningful. In the second set of experiments, high resolution spatial maps of the relative zinc composition were measured for the two samples. Fig. 4 shows two such maps, taken over small (sub-mm) regions at small step sizes of 10 μm. The spectrometer-grade detector has more uniformity in the zinc concentration than the poor-performance detector, as expected. The poor-performance one has a higher degree of mottling, or larger localized changes, as well as an overall gradual change from one side to the other.

*Tri-axial X-ray Diffraction (TAXRD)*

X-ray diffraction is a useful method for studying the crystallinity and lattice parameters of materials. In this work a high-resolution, tri-axial x-ray diffraction system was used. From the lattice parameters calculated from the XRD data, one can estimate the zinc composition. Here again, however, there is some uncertainty in the quantitative relation of this parameter to zinc composition.
For these measurements, a different set of comparable CZT detectors was used. Fig. 5 shows the XRD-measured zinc fraction at three points for the two samples. As can be seen, once again the poor-performance sample exhibits more zinc variation on the scale of the detector dimensions.

The tri-axial x-ray diffraction method allows for the separation of the diffraction peak broadening effects due to strain from changes in lattice parameter from those due to tilt from mosaicity. One can form the reciprocal space maps (RSM) of the samples which give a contour map of the intensity versus strain and tilt. Fig. 6 shows the RSMs of the (111) reflection for these two detectors. As can be seen, the poor-performance detector has a much higher amount of tilt than the spectrometer-grade detector. However, the spectrometer-grade detector does seem to exhibit a larger amount of strain, which would seem to indicate some level of compositional inhomogeneities. It appears that in this case the poor-performance detector is more limited by crystallinity problems.

Summary

In this work several materials characterization methods were performed on "good" and "bad" detectors to gain an understanding of the properties that limit the performance of large volume cadmium zinc telluride gamma-ray detectors. In particular, by using infrared transmission microscopy, particle-induced x-ray emission, photoluminescence, and tri-axial x-ray diffraction techniques it was found that poor-performance material exhibited larger variations in zinc composition and crystallinity than spectrometer-grade crystals. Efforts must be made to reduce these inhomogeneities if one wants to have high-quality large volume CZT gamma-ray spectrometers.

Acknowledgments

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References


Figure Captions

1. Spectrum of $^{137}$Cs taken with a 1 cm$^3$ Cd$_{0.9}$Zn$_{0.1}$Te detector, showing the "hole-tailing" effect.

2. Infrared transmission microscopy images (a) and proton-induced x-ray emission maps (b) on the same 2.5 mm x 2.5 mm region for spectrometer-grade and poor-performance CZT detectors. The IR images have been inverted, such that the dark regions indicate places of high transmission, while the PIXE image pixels are darker for a higher Zn/(Cd+Te) ratio.

3. Near band-edge low temperature (4.2K) photoluminescence spectra of the spectrometer-grade and poor-performance CZT detectors, and the width of the neutral-donor-bound exciton peak (D0-X) for each.

4. Maps of the relative zinc compositional changes in the spectrometer-grade and poor-performance detectors, as measured with room-temperature photoluminescence. The step size was 10 μm in the two dimensions.

5. Variation of the zinc fraction for the spectrometer-grade and poor-performance detectors, as determined from x-ray diffraction. The measurement points were spaced about 3 mm apart.

6. Reciprocal space maps of the spectrometer-grade and poor-performance detectors taken with tri-axial x-ray diffraction. The maps give a contour of the intensity versus the strain (change in lattice parameter from zinc variations) and the tilt (mosaicity in the crystal structure).
Spectrometer-Grade

(a) Poor-Performance  (b)
**Spectrometer-Grade**
\[ \Delta E/E_0 = 1.8 \times 10^{-3} \]

**Poor-Performance**
\[ \Delta E/E_0 = 3.3 \times 10^{-3} \]