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Analysis of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ Microstructure

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ABSTRACT

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The microstructure and chemical inhomogeneities of commercially available $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ (CZT) have been evaluated using electron microscopy and microanalytical techniques. Since imperfections, such as inclusions, cracks and extended crystallographic defects are known to affect the performance of CZT gamma-ray spectrometers, understanding the nature and origins of such imperfections is vital to the improvement of device performance. CZT that is grown using a high-pressure Bridgeman method has a polycrystalline microstructure that contains numerous grain boundaries, twins and inclusions. In this study, scanning electron microscopy and X-ray energy-dispersive spectroscopy were used to analyze inclusions and cracks inside CZT material. Such analysis found regions of material rich in C, O, Si, Zn and Te. Transmission electron microscopy revealed small subgrains and thin platelets of a second phase material located inside the large-grain CZT matrix. Details of these microstructural features and their possible origins are discussed.

Keywords: CdZnTe, electron microscopy, inclusions, microstructure, gamma-ray detectors

1. INTRODUCTION

$\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ (CZT) is a leading material for the application of room-temperature gamma-ray spectrometers.¹ CZT possesses the necessary material properties of high bulk resistivity, good photoconductivity and acceptable electron and hole transport, that are required to fabricate gamma-ray detectors. Unfortunately, chemical inhomogeneities (e.g. impurities and inclusions) and microstructural defects (e.g. grain boundaries and twins) adversely affect the properties for which CZT is sought. This study explores the microstructural features of commercially available CZT and discusses their possible origins.

Commercially available CZT is typically manufactured using a high-pressure Bridgeman (HPB) technique.² In this method, the use of high pressure inhibits evaporation of the charge and allows for a choice of crucible materials. Material prepared by this method has a polycrystalline microstructure that contains numerous inhomogeneities including grain boundaries, twins, cracks and inclusions. Across the length of the boule, variations in Zn composition occur due to a Zn segregation coefficient greater than unity.³ A uniform Zn concentration is important for device performance and can be attained by cropping off and discarding the ends of the boule. Several studies have investigated the inhomogeneities of CZT prepared by the HPB technique.³⁻⁷ In general, these studies have focused on inclusions, impurities, variations in Zn content and crystal defects.

Cracking of the CZT boule is a significant problem. Estimates suggest that up to 25% of the material produced by the HPB technique is lost due to cracks.⁸ Cracks are assumed to be the result of thermal stress developed during growth, but the exact origins of the cracks and reasons for their location are not

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known. Since cracks are internal free surfaces, they can act as sites for the accumulation of impurities and precipitates. The structural and chemical nature of the cracks makes these regions unusable for device application. The study of the microstructure and chemistry near the cracks may lend insight into the time when the cracks formed and to the reasons for the location of the cracks.

Another major inhomogeneity found in CZT boules are inclusions. Inclusions inside CZT are believed to be primarily metallic Te and Cd and have been categorized by Sen et al. into two classes: 1) star-shaped Cd inclusions and 2) triangular, hexagonal and irregular shaped Te inclusions.⁴ Second phase inclusions such as Te are attributed to the high defect concentration of CZT near its melting temperature.⁹ Justification for why these precipitates should contain either Te or Cd can also be based on the phase diagram of the Cd-Te-Zn system.¹⁰ For example, if a melt that was rich in Te were to solidify, the phase diagram would predict the formation of solid CZT and Te. These types of inclusions preferentially form near grain boundaries.⁶ Grain boundaries may act as low-energy nucleation sites for precipitation to occur. The density of these Te and Cd inclusions can be significantly reduced by post-growth annealing treatments.⁹

Besides solid inclusions of Te and Cd, CZT boules are suspected to have gaseous inclusions or voids.⁶ Gaseous phases may arise from incorporation of gases during high-pressure processing or from impurities in the CZT. Impurities inside CZT arise from the source materials and the processing conditions. For example, Te source material often contains CO₂, H₂O, N₂ and O₂.^{1,3} Manufacturers of CZT take several measures in order to reduce the amounts of gaseous contaminants in Te since these contaminants have been linked with an increased density of twins and microtwins.^{3,11} Voids and tubes have also been observed in related materials systems. For example, in the production of ZnSe crystals voids and tubes were found to contain nitrogen gas that was incorporated from the atmosphere in the growth chamber.¹²

In general, the incorporation of many of the microstructural inhomogeneities such as inclusions and extended defects during growth of CZT are not well understood. More research in determining the origins of these inhomogeneities must be completed in order to improve the quality of the CZT and thereby improve device performance. In this study several microscopic methods are used to better understand the nature of these types of defects.

2. EXPERIMENT

Polycrystalline CZT material, manufactured using HPB techniques, was obtained from commercial suppliers for analysis. The exact details of the HPB processing conditions were not disclosed. CZT samples were characterized using visible light microscopy (VLM), transmission infrared microscopy (IR), scanning electron microscopy (SEM), X-ray energy dispersive spectroscopy (XEDS) and transmission electron microscopy (TEM). A variety of techniques were used to characterize each type of microstructural feature. This approach should allow for an easy comparison between structures viewed by both IR and VLM with electron microscopy analysis. Prior to examining by VLM, IR and SEM, CZT samples were polished using one micron alumina slurry and a felt cloth. TEM samples were prepared using conventional dimpling and ion milling techniques. A JEOL 6400 field-emission SEM, operating at 10 keV and equipped with a windowless Noran XEDS detector, and a JEOL 840, operating at 15 keV and equipped with a ultra-thin window Noran XEDS detector, were used for SEM analysis. A JEOL 4000EX, operating at 400 keV, was used for TEM analysis.

3. RESULTS AND DISCUSSION

3.1 Large-scale structural/grain features

Fig. 1 is a schematic illustration of a cross-section of a CZT boule. This illustration is based on VLM observations of several CZT samples and shows the microstructural features common to material prepared by HPB. This illustration shows cracks that radiate inward from the sides of the boules. Such cracks vary in size and are random in location. Twins and grain boundaries are also common. Twins typically extend from both the edge of grains boundaries and the edge of the boule and terminate inside the bulk of a grain. This suggests that grain boundaries and the edge of the boule act as initiation sites for the formation of twins. Grain boundaries generally contain both curved and faceted regions.

Fig. 1 Schematic illustration of a CZT boule. This image shows a typical microstructure containing grain boundaries (GB), twins (TW) and cracks (CR).

Grains in CZT are typically a few centimeters in size. Within these large grains, isolated subgrains were observed using TEM analysis. Fig. 2 is a pair of TEM images that show a subgrain which has formed inside of a larger CZT grain. Such subgrains have been observed in CZT boules and found to have high concentrations near the boule edges.³ Thermal stresses which develop near the boule edges have been speculated as to the cause of the subgrains.³ With subgrains being only 100 nm's in size, the difference in size between the grains and the subgrains is five orders of magnitude. Preliminary TEM analysis has indicated distinct crystallographic alignments between the grains and subgrains. Most of the microstructural features of the CZT are much larger than these subgrains. This study will start by addressing some of these larger features, such as cracks and inclusions.

Fig. 2 a) Bright-field TEM image of a CZT subgrain. b) Corresponding dark-field TEM image formed with a reflection unique to the subgrain.

3.2 Cracks

Fig. 3a is a secondary-electron SEM image that shows a crack running through a CZT boule. This particular crack extends approximately 2 cm into the sample. The path of the crack was not associated with grain boundaries or twins. At several locations along the crack, regions of microcracks had formed and the crack direction was observed to abruptly change. Closer observation of the crack with the SEM revealed the crack to be filled with a material that contained a yet smaller crack. The second phase material inside and near the crack was found to vary in amount and composition. Fig. 3a shows a typical region of this second phase material. XEDS analysis revealed this region of material to contain increased amounts of C, O and Zn as compared with the surrounding matrix. Figs. 3b and 3c show the corresponding XEDS spectra from the CZT matrix and the material inside the crack, respectively. Besides C, O and Zn, regions rich in Te and Si were also observed along the length of the crack.

The accumulation of this second-phase material inside the crack may have occurred during growth or during post-growth processing, such as cutting. Several different explanations of the existence of this material can be made. If the crack formed during growth, a second phase of liquid or gas may have infiltrated the crack and resulted in the deposited material. The crack may have also acted as a site for the accumulation of impurities and precipitates. The location of the crack may be a result of the crack forming along preexisting impurities and precipitates. Fig. 4 is an IR image showing the same crack and the surrounding region. IR imaging of the area around the crack found the crack to follow a region of material that was less transparent to the IR light. This darker region may contain a change in composition or a higher density of precipitates, both of which are currently under investigation. Future research will probe the response of CZT detectors near cracks and work to correlate these observations with the results of microstructural analysis.

Fig. 3 a) Secondary-electron SEM image showing a crack running through a piece of CZT. b) XEDS spectrum taken from the CZT matrix. c) XEDS spectrum taken from the material found inside the crack. This spectrum shows the material to be rich in C, O and Zn.

Fig. 4 is an IR image showing a crack in a CZT boule. The crack tended to follow a darker region in the CZT, as labeled in the figure.

Evidence for microcracking of the CZT boule during growth was also observed. Fig. 5 is a bright-field TEM image showing a platelet of second phase material inside a CZT grain. This platelet followed specific crystallographic directions, namely the $[100]$ and $[1\bar{1}1]$ directions in CZT. Selected area diffraction showed the interior material to be polycrystalline, although interference due to the intense single crystal spots of the adjacent CZT prevented definitive phase identification. The platelets separate regions of CZT that are within 2° of the same crystal orientation of each other, as determined by electron diffraction. This observation suggests that the platelets are internal to large CZT grains. The platelets were found to form on $\{110\}$ type planes, which is a cleavage plane in CZT. Since cracks, in general, tend to follow cleavage planes, one possible explanation is that these features are the result of microcracks that were infiltrated with a liquid during growth. Identification of the phase and chemical identity of these features is required to support this hypothesis.

3.3 Inclusions

Commonly, samples of CZT prepared by the HPB technique contain inclusions. These inclusions vary in size, shape and distribution and are often assumed to contain either metallic Te or Cd. Fig. 6 is a pair of IR images that show inclusions formed inside CZT. IR microscopy is a useful technique for analyzing inclusions since CZT is transparent to infrared light. Inclusions, which either scatter or absorb the infrared light, appear dark in these images. Fig. 6a shows an example of an isolated inclusion that has an irregular shape. Often these inclusions are found in large clusters and along specific directions.⁶ This phenomenon is likely the result of the inclusions forming along grain boundaries in the material. Fig. 6b shows a different type of inclusion which is shaped like a rod. These rod-shaped features are commonly observed in CZT samples and most often form along the direction of crystal growth. An important question is whether these elongated features are composed of metallic Te or Cd, similar in nature to the other observed inclusions, or whether these features are composed of other types of material, such as entrapped gases from the high pressure processing.

Fig. 5 is a bright-field TEM image showing a platelet of second phase material running through a CZT grain.

In order to help answer the question as to the origins and make up of these rod-shaped features in CZT, a specimen was prepared from the sample shown in Fig. 6b. The side of the sample from which the rod intersected was polished, and the end of the sample was analyzed using SEM and XEDS techniques. Fig. 7a is a secondary-electron SEM image of the surface of a cross-section of the rod-shaped feature and shows the tube to be filled with material. XEDS and mapping of this region were used to determine the chemical nature of this material. Figs. 7b, 7c and 7d are X-ray maps that show the spatial distribution of C, Cd and Te, respectively. XEDS analysis found the material inside the tube to consist primarily of C. Fig. 8 shows XEDS spectra taken from the CZT matrix and the material inside the rod. Only small amounts of other elements such as Cd and Te were detected.

There are several possible scenarios for how the material inside the rod formed. Whether this material accumulated inside the tube during growth or during post-growth processing, such as cutting, is not known. If the C-rich material were to form during growth of the CZT boule, the graphite crucibles that are used for growth could act as the source for C. VLM imaging showed that the rod was located at a grain boundary inside the CZT. A grain boundary could act as a nucleation site for the formation of a second phase, gaseous or solid. Further research is underway to determine the exact origins of the C-rich material and to determine the effects of the rods on device performance. Currently, some manufacturers of CZT tend to cut the boules along the growth direction in order to keep the direction of the rods in the plane of their detectors. Rods which transverse the detector, i.e. connect electrodes on either side of the detector,

are believed to be detrimental to device performance. Certainly, if the rod were to contain a conductive media such as Au or C the rod would act as a short circuit for the device. This research has shown that the rod-shaped features are not filled with metallic Te or Cd.

Fig. 6 a) IR image of an irregular shaped inclusion. b) IR image showing a rod shaped feature.

4. SUMMARY

The microstructure of CZT boules grown using HPB methods has been characterized by electron microscopy and microanalytical techniques. This study found commercially available CZT to contain large-scale microstructural features such as inclusions and cracks. Local chemical analysis of these structures by XEDS revealed regions rich in a variety of elements including C, O, Si, Zn and Te. Speculations on the origins of these materials were discussed. This research has shown that the rod-shaped features in CZT are not filled with metallic Te or Cd. TEM analysis of the CZT revealed small subgrains and platelets that were found to be internal to the large CZT grains. Future research will continue to characterize the microstructure of the CZT boules and will also work to link these microstructural observations with device performance.

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Fig. 7 a) Secondary-electron SEM image (SEI) showing the end of the rod and the material inside the rod. XEDS maps showing the spatial distribution of b) C, c) Cd and d) Te. The brighter regions of the maps represent regions with larger amounts of the stated element.

Fig. 8 a) XEDS spectrum taken from the CZT matrix. b) XEDS spectrum taken from the material found inside the rod. This spectrum shows the contents of the rod to consist primarily of C.

REFERENCES

- 1 R. B. James, T. E. Schlesinger, J. Lund, and M. Schieber, "Cd_{1-x}Zn_xTe Spectrometers for Gamma and X-Ray Applications," in *Semiconductors and Semimetals*, eds. T. E. Schlesinger and R. B. James, **40**, pp. 335-381, Academic Press, 1995.
- 2 F. P. Doty, J. F. Butler, J. F. Schetzina, and K. A. Bowers, "Properties of CdZnTe crystals grown by a high pressure Bridgeman method," *J. Vac. Sci. Technol. B*, **10**, pp. 1418-1422, 1992.
- 3 S. Sen and J. E. Stannard, "Improved quality of bulk II-VI substrates for HgCdTe and HgZnTe epitaxy," *Mat. Res. Soc. Symp. Proc.*, **302**, pp. 391-401, 1993.
- 4 S. Sen, S. C. Liang, D. R. Rhiger, J. E. Stannard, and H. F. Arlinghaus, "Reduction of CdZnTe substrate defects and relation to epitaxial HgCdTe quality," *J. Electronic Mat.*, **25**, pp. 1188-1195, 1996.

- 5 J. Shen, D. K. Aidun, L. Regel, and W. R. Wilcox, "Characterization of precipitates in CdTe and $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ grown by vertical Bridgeman-Stockbarger technique," *J. Crys. Growth*, **132**, pp. 250-260, 1993.
- 6 C. J. Johnson, E. E. Eissler, S. E. Cameron, Y. Kong, S. Fan, S. Jovanovic, and K. G. Lynn, "Crystallographic and metallurgical characterization of radiation detector grade cadmium telluride materials," *Mat. Res. Soc. Symp. Proc.*, **302**, pp. 463-478, 1993.
- 7 H. R. Vydyanath, J. A. Ellsworth, J. B. Parkinson, J. J. Kennedy, B. Dean, C. J. Johnson, G. T. Neugebauer, J. Sepich, and P. K. Liao, "Thermomigration of Te precipitates and improvement of (Cd,Zn)Te substrate characteristics for the fabrication of LWIR (Hg,Cd)Te photodiodes," *J. Electronic Mat.*, **22**, pp. 1073-1080, 1993.
- 8 C. Szeles, "Yield-limiting factors in HPB CdZnTe growth," reported at 5th Scientific Symposium on Room-Temperature Semi-Conductor X-ray, Gamma-ray and Neutron Detectors, 1997.
- 9 H. R. Vydyanath, J. Ellsworth, J. J. Kennedy, B. Dean, C. J. Johnson, G. T. Neugebauer, J. Sepich, and P.-K. Liao, "Recipe to minimize Te precipitation in CdTe and (Cd,Zn)Te crystals," *J. Vac. Sci. Technol. B*, **10**, pp. 1476-1484, 1992.
- 10 J. Steininger, A. J. Strauss, and R. F. Brebrick, "Phase Diagram of the Zn-Cd-Te Ternary System," *J. Electrochem. Soc.*, **117**, pp. 1305-1309, 1970.
- 11 S. L. Bell and S. Sen, "Crystal growth of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ and its use as a superior substrate for LPE growth of $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$," *J. Vac. Sci. Technol. A*, **3**, pp. 112-115, 1985.
- 12 K. Terashima and M. Takeda, "Typical macroscopic defects in ZnSe crystals grown from the melt," *J. Crys. Growth*, **110**, pp. 623-625, 1991.