Structural and Chemical Analysis of Grain Boundaries and Tellurium Precipitates in Commercial $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$

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ABSTRACT

The structure and chemistry of grain boundaries in commercial $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$, prepared by the high-pressure Bridgman technique, have been analyzed using transmission electron microscopy, scanning electron microscopy, infrared-light microscopy and visible-light microscopy. These analyses show that the grain boundaries inside the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ materials are decorated with tellurium precipitates. Analysis of a tellurium precipitate at a grain boundary by transmission electron microscopy and selected-area electron diffraction found the precipitate to consist of a single, saucer-shaped grain. Electron diffraction from the precipitate was consistent with the trigonal phase of tellurium (space group $P3_121$), which is the equilibrium phase at room temperature and atmospheric pressure. This precipitate was found to be aligned with one of the adjacent CZT grains such that the tellurium (011) planes were nearly parallel to the CZT (111) planes. High-resolution transmission electron microscopy of the $\text{Te}/\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ interface showed no tertiary phase at the interface. The structures of the grain boundaries and the $\text{Te}/\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ interface are discussed and related to their possible implications on $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ gamma-ray detector performance.

Keywords: CZT, Cadmium Zinc Telluride, Radiation Detector Materials, Tellurium Precipitates, Electron Microscopy

1. INTRODUCTION

Although $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ (CZT) is a leading material for use in gamma-ray spectrometer applications, the material that is currently available still suffers from structural inhomogeneities that lead to spatially varying electrical performance. Commercially available CZT is typically manufactured using a high-pressure Bridgman (HPB) technique¹. In this method, a large over-pressure of an inert gas (typically argon) is used to inhibit the evaporation of the charge material. Common structural defects include grain boundaries, twin boundaries, pipes, and second phase precipitates^{2,3}. Grains are typically on the order of centimeters in size. Precipitates are thought to arise due to the retrograde solubility in the Cd-Te phase diagram^{4,5,6}. As the CZT boule is cooled, tellurium and/or cadmium precipitates out of the CZT lattice. The chemistry of these precipitates is determined by whether the starting material is rich in tellurium or cadmium: tellurium precipitates form for charges that are rich in tellurium, which is the common starting charge for commercially available CZT.

These material problems impose size limitations on CZT based devices, hindering the efficient detection of high photon energies and weak radiation signals and impacting the development of radiation detector arrays. For instance, Doty *et al.* showed that CZT detector array pixels located near grain boundaries exhibit a significantly reduced efficiency compared to those located well away from grain boundaries⁷. These results suggest that the electric fields and charge collection inside the device are severely perturbed by the grain boundaries^{7,8}, although the precise reasons for this effect are unknown. In order to improve detector performance, advances in material quality must be obtained.

A critical step in improving the quality of and understanding variations in detector performance is to characterize the nature of the structural inhomogeneities. In this paper we investigate the microstructure of high-pressure Bridgman grown CZT with an emphasis on the nature of internal interfaces and their relation to second phase formation. Such interfaces can potentially serve as segregation sites for impurities and/or excess tellurium. In CZT it is unknown whether such segregation leads only to the formation of discrete, isolated precipitates, or whether a continuous, intergranular phase results. Furthermore, although there have been a number of studies of the composition and distribution of tellurium precipitates in CdTe and CZT, grown by either HPB or conventional Bridgman techniques^{3,9-17}, structural details of the individual precipitates, including the crystallographic phase, remain unclear.

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2. EXPERIMENTAL DETAILS

Polycrystalline CZT was obtained from commercial suppliers for analysis. This material was grown by the HPB method using a starting charge that was rich in tellurium and contained a nominal zinc concentration of 10%. An over pressure of argon was used to suppress the loss of cadmium from the melt. Additional parameters related to the growth and cooling rates were not disclosed by the manufacturer. Several complementary microscopic methods, including visible-light microscopy (VLM), transmission infrared-light microscopy (IR), scanning electron microscopy (SEM), X-ray energy-dispersive spectroscopy (XEDS) and transmission electron microscopy (TEM) were used to characterize the CZT samples. Prior to examination by VLM, IR and SEM, the CZT samples were polished using a one-micron alumina slurry and a felt cloth. TEM samples were prepared using conventional dimpling and ion milling techniques. A JEOL 840 SEM, operating at 15 keV and equipped with a Noran XEDS detector, was used for SEM and XEDS analysis. Transmission electron microscopy characterization was conducted using a JEOL 1200EX conventional TEM, operating at 120 keV, and a JEOL 4000EX high resolution TEM, operating at 400 keV.

3. RESULTS AND DISCUSSION

3.1. DISTRIBUTION AND MORPHOLOGY OF TELLURIUM PRECIPITATES

The distribution of extended crystallographic defects and the second phase precipitates are closely related. Extended defects provide low-energy nucleation sites for the precipitation of tellurium during the cooling stage of the HPB process. For this reason, grain boundaries in CZT typically contain a higher density of precipitates than the bulk material. An example is presented in Figure 1, which shows a VLM image of a CZT grain boundary that is decorated with a high density of second phase particles protruding from the surface. XEDS analysis showed that these features are tellurium rich (*e.g.*, see Figure 3b). Such boundaries can be seen in the VLM due to the anisotropic polishing of the alumina slurry. Here, grains of CZT polish at different rates depending on their relative orientation to the surface. Likewise, precipitates of a different phase and chemistry than the CZT will also be visible at the surface. Depending on the type of polishing procedure used, the tellurium precipitates may cause surface roughness. This has implications for detector fabrication processes, where surface roughness can be detrimental to the application of metal contacts. A three dimensional perspective of the distribution of tellurium precipitates can be acquired using IR imaging. Since CZT is transparent to IR light, internal defects that act to either scatter or absorb the IR light, such as precipitates, voids and cracks, show contrast as dark features in the IR image. Figure 2 shows a transmission IR image of the grain boundary shown in Figure 1. As shown in the schematic at the bottom of Figure 2, the interface traverses the CZT slab and is inclined relative to the imaging direction. The precipitates are evenly distributed along this particular grain boundary.

The morphology of the interfacial precipitates is shown more clearly at the higher magnifications available in the electron microscope. Figure 3a is a secondary-electron SEM image of a precipitate located along the grain boundary shown in Figures 1 and 2. XEDS spectra (Figure 3b) from the CZT matrix and particle, confirmed that the precipitate was tellurium rich. Light elements, such as oxygen, were not detected in the XEDS spectra due to the use of a beryllium window on the XEDS detector. Constituents other than the three starting materials (cadmium, tellurium, and zinc) were not detected. The SEM image shows clearly the saucer-shaped morphology of the precipitate, which is elongated parallel to the interface. This morphology was typical of precipitates observed along grain boundaries. In contrast, precipitates located in the bulk of the CZT, as well as along twin boundaries, tended to have a faceted polyhedral shape. Although precipitation also occurred along twin boundaries, in most cases grain boundaries possessed a higher density of precipitates. This observation suggests that the barrier for nucleation of a tellurium precipitate at a grain boundary is generally less than that for the twin boundary. Nevertheless, the distribution of interfacial tellurium precipitates varied between different grain boundaries; indeed some grain boundaries were found to be completely free of precipitates. Thus, as the character of the grain boundary changes, the barrier for nucleation also changes. Locations where grain boundaries met (*i.e.* triple junctions) possessed some the highest concentrations of precipitates. Often, these triple junctions contained a single continuous precipitate of tellurium. If such a precipitate were to traverse the entire detector it could act as a wire, providing a short circuit path with obvious adverse impact on detector performance.

Figure 3a. Secondary-electron SEM image of a tellurium precipitate located along a grain boundary in CZT.

Figure 3b. XEDS spectra from the region shown in Figure 3a. Top spectrum: Matrix. Bottom spectrum: precipitate.

Figure 1. Visible-light micrograph of grain boundary intersecting the surface of a CZT specimen. The grain boundary is decorated with precipitates.

Figure 2. Infrared transmitted light image showing precipitates decorating a CZT grain boundary. The schematic shows the three-dimensional distribution of the precipitates.

Figure 4. Selected area electron diffraction obtained from a precipitate located at a CZT grain boundary. The measured lattice spacings and interplanar angles from this pattern and from patterns taken along other zone axes are consistent with those expected for the room temperature, atmospheric pressure phase of tellurium (trigonal structure, space group $P3_121$). This pattern is for a $[\bar{1}2\bar{1}3]$ zone axis.

Figure 5. High-resolution TEM image taken at the interface between the tellurium precipitate and the CZT matrix. This image shows the alignment between the CZT (111) (3.7 Å) and Te (0 $\bar{1}$ 11) (3.2 Å) planes. For this image, the sample is oriented along a CZT $[\bar{1}1\bar{2}]$ direction with the Te precipitate close to a $[5\bar{1}43]$ direction.

3.2 TELLURIUM PRECIPITATE PHASE IDENTIFICATION AND MICROSTRUCTURE

Previous work on precipitate phase identification in CdTe-based materials has focused on Bridgman grown CdTe. Although the tellurium phase that is stable at ambient conditions (room temperature and atmospheric pressure) is a trigonal structure (space group $P3_121$, $a=4.458$ Å and $c=5.927$ Å), isomorphic with selenium^{18,19,20}, several different phases have been identified in these previous studies: Yokota *et al.*¹⁷, identified tellurium precipitates in the trigonal phase, Rai *et al.*¹⁴ reported an hexagonal close-packed phase, and Shin *et al.*¹³ reported the high-pressure rhombohedral phase, a structure that normally exists only at pressures above 70 kbar¹⁰.

The phase of the tellurium precipitates in the HPB CZT sample considered in the present study was investigated using transmission electron microscopy. A selected area electron diffraction pattern from a precipitate located along a CZT grain boundary is shown in Figure 4. The measured lattice spacings and interplanar angles from this pattern, and from patterns taken along other zone axes, are consistent (within ~3%) with those expected for the trigonal structure (i.e., the room temperature, atmospheric pressure phase). The pattern in Figure 4 is for a $[\bar{1}2\bar{1}3]$ zone axis. The microstructure of the precipitate consisted of a single tellurium grain, which contained dislocations and voids. Voids in tellurium precipitates have been postulated to be associated with the accumulation of vacancies during the precipitation of tellurium in CdTe materials²¹.

Figure 5 is a high-resolution TEM image of the interface between the tellurium precipitate and the CZT matrix. For this image, the sample is oriented along a CZT $[\bar{1}1\bar{2}]$ direction with the tellurium precipitate close to a $[5\bar{1}43]$ direction. The lattice fringes in the image, as well as selected area electron diffraction (not shown), show an alignment between the CZT (111) (3.7 Å) and the tellurium (0 $\bar{1}$ 11) (3.2 Å) planes. The mismatch in lattice spacing between these two planes is 14%. Alignment of planes that are closely matched in lattice spacing is a way for the system to minimize the interfacial energy

between the precipitate and matrix. Diffraction analysis of the interface between the tellurium precipitate with the other CZT grain did not reveal a particular crystallographic alignment. The HRTEM image shows that the interface between the tellurium precipitate and the CZT is abrupt. No tertiary phase layer was observed at the interface. Impurities in the CZT may be expected to accumulate at such an interface. XEDS analysis was used to probe the chemistry of the precipitate in the TEM, but no conclusive evidence for the accumulation of impurities at the Te/CZT interface or in the tellurium precipitate was obtained.

3.3 CHARACTER OF THE CZT GRAIN BOUNDARIES

An important question in the study of CZT is whether high-angle grain boundaries contain a secondary phase at the interface. A secondary phase may have significant effects on the electrical properties of the boundary. Since tellurium has been identified as a secondary phase at grain boundaries, one question is whether the precipitates are localized or whether in addition there is a thin, but continuous, interlayer of tellurium (or another phase) along the grain boundary. These two microstructural pictures would have different implications for the effect of the grain boundaries on detector performance since in the latter case there would be a continuous sheet of conductive material along the interface. Figure 6 is a high-resolution TEM image of a CZT grain boundary. The image is from the same grain boundary as the tellurium precipitate shown in Figure 5, but is from a region well separate from the precipitate. Figure 6 shows lattice fringes from the planes of both CZT grains. Each grain has a different orientation with respect to the electron beam such that (220) fringes are imaged on the left side and the (111) fringes are imaged on the right side. The interface between the two crystals is abrupt with no evidence for the presence of a secondary interfacial phase.

Figure 6. High resolution TEM image of a CZT grain boundary. The (220) (2.3Å) and (111) (3.7Å) lattice fringes are visible in the left and right crystals, respectively. The image shows that the interface is sharp to within less than 10 Å with no evidence for any continuous secondary phase separating the two grains.

4. CONCLUSIONS

The microstructure and internal precipitates of commercially available CZT, grown by the high-pressure Bridgman (HPB) method, have been characterized. Grain boundaries were found to be decorated with tellurium precipitates. TEM analysis identified the tellurium precipitate phase as the trigonal form (space group $P3_121$), which is the equilibrium phase of tellurium at room temperature and atmospheric pressure. This precipitate was found to be aligned with one of the adjacent CZT grains and was found aligned with the tellurium $(0\bar{1}11)$ planes nearly parallel to the CZT (111) planes. High-resolution TEM analysis of the Te/CZT interface found no tertiary phases separating the two materials. For regions of the grain boundary that are located at a relatively far distance away from the tellurium precipitate, the grain boundary was found to be relatively sharp (within less than $10 \text{ \AA}$ in width). No secondary or amorphous phases were observed at the grain boundary.

ACKNOWLEDGMENTS

This work is supported at Sandia National Laboratories under contract number DE-AC04-94-AL85000. The authors acknowledge the financial support of the U. S. Department of Energy, Office of Nuclear Non-Proliferation, NN-20.

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