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MnTe Purification***

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# Improvement of CdMnTe Detector Performance by MnTe Purification

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## ABSTRACT

Residual impurities in manganese (Mn) are a big obstacle to obtaining high-performance CdMnTe (CMT) X-ray and gamma-ray detectors. Generally, the zone-refining method is an effective way to improve the material's purity. In this work, we purified the MnTe compounds combining the zone-refining method with molten Te, which has a very high solubility for most impurities. We confirmed the improved purity of the material by glow-discharge mass spectrometry (GDMS). We also found that CMT crystals from a multiply-refined MnTe source, grown by the vertical Bridgman method, yielded better performing detectors.

## INTRODUCTION

Although the physical properties of CdMnTe (CMT) and CdZnTe (CZT) are very similar, CMT crystals show poorer performance as X-ray and gamma detectors; furthermore, controlling their electrical properties was very difficult due to the high concentrations of residual impurities arising from the impure starting materials [1,2]. Despite these drawbacks, one important difference favoring the usage of CMT rather than CZT is the fact that segregation coefficient of Mn in the CdTe host is close to 1, thereby ensuring a uniform alloy composition within large-volume ingots. Reportedly, cadmium vacancies in CdTe-based semiconductors are successfully compensated by doping with indium, chlorine, or aluminum [1,2].

The concentration of native point defects (NPDs) in CdTe crystals at room temperature (RT) is about  $10^{13} - 10^{15} \text{ cm}^{-3}$  [3,4]. Maintaining a concentration of residual impurities below this level ensures their minimal effect on the crystals' electrical properties. Typically, the most effective way to minimize uncontrollable impurities overall has been by combinations of repeated vacuum-distillation and zone-refining [4,5]. Such methods resulted in impurity contents as low as  $10^{15} - 10^{16} \text{ cm}^{-3}$ , depending upon the particular impurities. In our experiment, we improved the purity of MnTe via the molten Te zone-refining method, and verified it in the better performance of the resulting CMT detector.

## EXPERIMENT

The CMT:In crystals were grown by the vertical Bridgman method using a mixture of CdTe (6N), MnTe, and excess Te. At high temperatures, Mn readily reacts with the quartz tubing even if its inner wall is completely carbon coated. The MnTe was synthesized at 1026 C at Te-rich conditions, i.e., with 44% of Mn (4N) and 56% of Te (6N). The source manganese first was cleaned with diluted  $\text{HNO}_3$  in methanol. Then, vitreous graphite tubing containing Mn and Te was loaded in quartz tube, and sealed under a vacuum of  $10^{-6}$  torr. Then, the temperature was raised at a rate of 0.5 C/min to 960 C to avoid uncontrolled exothermic reactions, and maintained there for one week until the reaction was completed. Finally, we raised the temperature to 1026 C and held it there for 24 hours. We charged the synthesized MnTe in the carbon-coated quartz

ampoule with suitable amounts of Te in accordance to the phase diagram and temperature [6]. The heating zone was set to 800 C, and then the ampoule was translated vertically at a speed of 6 mm/day. The effectiveness of zone-refining was verified by glow-discharge mass spectrometry (GDMS).

Four CMT samples of two different sizes,  $10 \times 10 \times 2$ - and  $4 \times 4 \times 11$ -mm<sup>3</sup>, were prepared from the ingots. The resistivity of those samples was about  $2\text{-}4 \times 10^{10}$   $\Omega$ -cm. The extended defects in samples were inspected via White X-ray Beam Diffraction Topography (WBXDT) [7], a technique frequently employed to visualize growth- and process-induced defects, such as dislocations, twins, domains, and inclusions. The electrode was prepared by an electro-less method with 5% AuCl<sub>3</sub>. A standard eV Products test holder with a preamplifier, further shaped and amplified with a standard research amplifier, was employed to measure the <sup>241</sup>Am and <sup>132</sup>Cs gamma-ray signals, while keeping the temperature around 20 C. The gamma source was uncollimated, and shaping time was set as 2 micro-seconds.

## RESULTS AND DISCUSSION

Figure 1 is a cross-sectional view of an as-grown CMT ingot wherein the uniformity of Mn in a CMT slab was measured by micro X-ray fluorescence ( $\mu$ XRF). Usually, the high iconicity of CMT results in low stacking-fault energy, and thus, twins are generated readily. However, controlling growth conditions can prevent the generation of twins. For the first time, we demonstrated homogeneous Mn distribution throughout a whole CMT ingot.

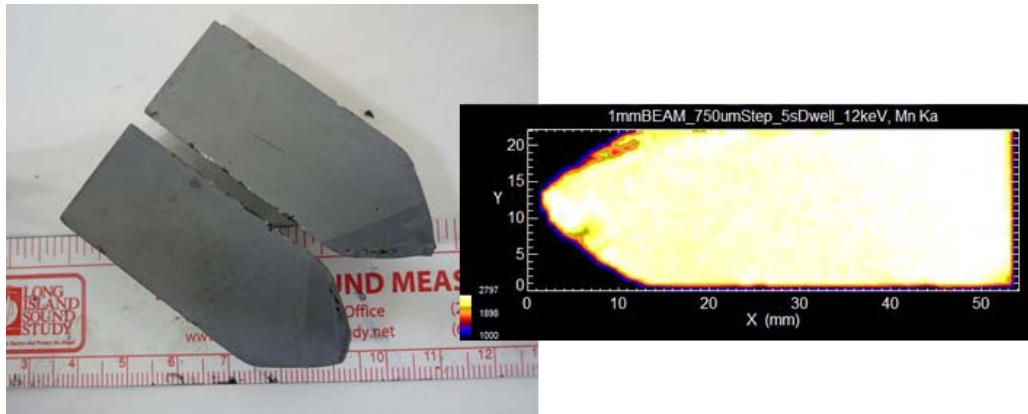


Figure 1 Cross-sectional view of the 1-inch diameter CMT ingot and the Mn uniformity in the CMT slab. The whole area is one single grain except for the first-to-freeze part. The  $\mu$ -XRF measurements were acquired at BNL's NSLS X-27a beamline over a  $55 \times 22$  mm<sup>2</sup> area with a 750-  $\mu$ m step.

With WBXDT, we can gain information on the type and distribution of structural defects, such as dislocations, inclusions/precipitates, stacking faults, growth-sector boundaries, twins, and low-angle grain boundaries in single-crystal materials. The principle of X-ray topography is the same as that of Laue diffraction. Passing the white synchrotron beam through a monochromator creates an X-ray topograph when the crystal is set to the Bragg angle for a specific set of lattice planes for the selected X-ray energy. Images from different atomic planes are acquired by orienting the sample to satisfy the Bragg condition for those planes, and orienting the detector to

the new scattering angle ( $2\theta_B$ ) to record the image. Depending on operational mode, the system can function in the transmission- or the reflection-mode. The transmission and the reflection modes, respectively, are used for investigating defects in the bulk and surface. Figure 2 shows typical WBXDT images of CMT crystals grown by the vertical Bridgman method. They contain many extended defects, such as low-angle grain boundaries, grain boundaries, and large (20-30  $\mu\text{m}$ ) Te inclusions.

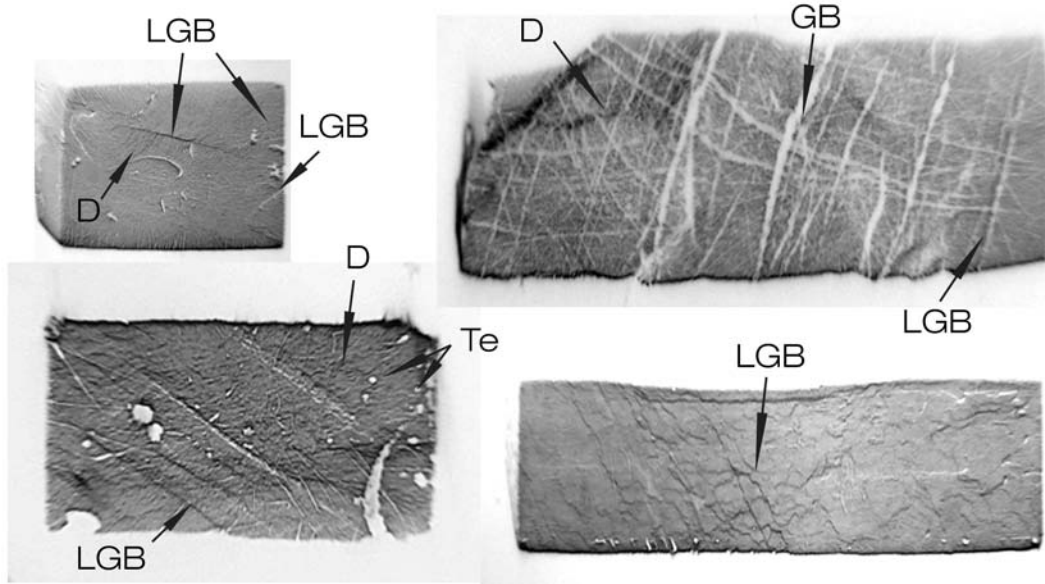


Figure 2 Typical WBXRD data from CMT crystals. They contain extended defects such as grain boundaries (GB), low-angle grain boundaries (LGB), dislocations (D), and Te inclusions (Te).

The segregation coefficient ( $k$ ) and solubility of elements in molten Te is a crucial factor in purifying raw material by molten Te zone-refining. In CdTe, except for group II elements, most elements have a segregation coefficient of less than 1, and close to 1 for Sn and Mn in CdTe. Table 1 summarizes the Glow-Discharge-Mass-Spectrometer (GDMS) analysis data on the just-synthesized and two times zone-refined MnTe. There are no data available on these kinds of impurities presented in MnTe/CMT material, on the segregation coefficient ( $k$ ) of impurities, and its effects on the electrical properties. The most abundant impurities present in synthesized MnTe with Mn (4N) and Te (6N) were Cu, Fe, Al, S, Mg, and Si. After purifying the MnTe using a Te solvent, these impurities were greatly reduced, as shown in Table 1. However, these impurities levels are still high. In our previous research, we found a photoluminescence (PL) peak located around 0.53 eV just in CMT samples [8]. Maybe one of these impurities is responsible for that PL peak.

Table 1. Concentrations of major impurities in MnTe before and after purification.

Elements	Before (ppm wt)	After (ppm wt)
Al	2.1	0.05
Cl	0.19	0.07
Cu	1.1	0.4
Cr	1.3	0.01
Fe	6	0.5

Mg	4.2	0.3
P	0.5	< 0.007
S	40	1.1
Se	0.9	0.04
Si	6	0.21
Zn	1	0.01

The electron mobility-lifetime product of the CMT detectors was calculated from the dependence of the peak channel number versus bias voltage by fitting the Hecht equation; the typical product was  $3\text{-}4 \times 10^{-3}$  cm/V. Figure 3 shows the gamma-ray response for the CMT detectors. For the first time, we obtained  $^{137}\text{Cs}$  spectra with large-volume CMT detector in virtual Frisch-grid configuration [9]. The energy resolution of 662 keV is about 2.1 %, and its value is comparable with that of a good CZT detector.

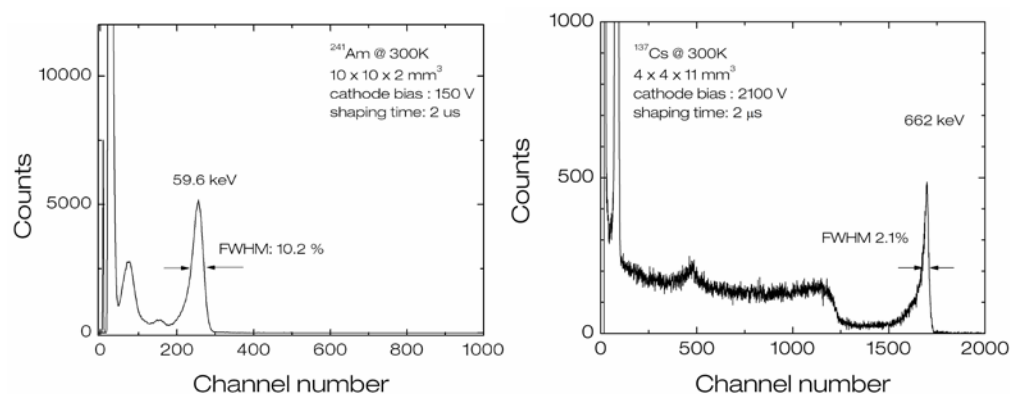


Figure 3 Gamma-ray response of the planar and bar-type virtual Frisch-grid CMT detectors for an  $^{241}\text{Am}$  and a  $^{137}\text{Cs}$  source. The size of the planar and bar-type detector, respectively, is  $10 \times 10 \times 2 \text{ mm}^3$  and  $4 \times 4 \times 11 \text{ mm}^3$ .

## CONCLUSIONS

The CMT ingots grown under optimized conditions by the vertical Bridgman method show nearly single-grain crystals and very uniform Mn distribution throughout the whole areas. A zone-refining method with molten Te solvent proved an effective way of enhancing material purity and the overall performance of the CMT detectors' performance. The major impurities existing in MnTe, i.e., Cu, Fe, Al, Mg, S, and Si, likely play a key role in electrical properties of CMT material; our refinement lowered their concentrations, and hence, improved the detectors' performances. More experiments will clarify the segregation tendency of these elemental impurities in MnTe- and CMT-materials.

## ACKNOWLEDGMENTS

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