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Raw Materians***

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Growth of CZT using additionally zone-refined raw materials

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ABSTRACT

Results will be presented for the growth of CdZnTe by the low pressure Bridgman growth technique. To decrease deep-level trapping and improve detector performance, high purity commercial raw materials will be further zone refined to reduce impurities. The purified materials will then be compounded into a charge for crystal growth. The crystals will be grown in the programmable multi-zone furnace (PMZF), which was designed and built at Northrop Grumman's Bethpage facility to grow CZT on Space Shuttle missions. Results of the purification and crystal growth will be presented as well as characterization of crystal quality and detector performance.

Keywords: CZT, CdZnTe, Bridgman, zone refining, purification, room temperature gamma-ray detector

1. INTRODUCTION

Cadmium Zinc Telluride (CZT) is currently the material of choice for high resolution, room temperature X-ray and gamma-ray detection. It has a suitable bandgap and electron mobility-lifetime product, but performance suffers from small grain size, Te inclusions [1], subgrain boundaries [2] and deep level trapping [3].

The purpose of this investigation is to reduce deep-level trapping by zone-refining high purity commercial raw materials and to decrease the subgrains in the crystal by the use of choked seeding. In the choked seeding technique, the seed pocket is connected to the conical tip and full ampoule diameter by a small capillary tube. The melt from the charge contacts the melted top layer of the seed and comes to thermal equilibrium. When translation is started, crystal growth starts from the seed and must pass through the capillary, which reduces the number of subgrain boundaries present in the resulting crystal.

2. EXPERIMENTAL

2.1 Zone refining

High purity (6N - 99.9999% pure) Cd, Zn and Te from 5N Plus, Inc. was used in this program. This material was additionally zone refined (hereafter to be referred to simply as 'zone refined') [4] at Northrop Grumman to reduce remaining impurities. The relevant material properties are shown in **Table I**. As expected, the metals (Cadmium and Zinc) have a much higher thermal conductivity than Tellurium, which can make zone refining more difficult due to problems in keeping multiple zones separated. All three materials have moderate melting points, which make processing them in quartz ampoules convenient. Cd, Zn and Te also have substantial vapor pressures of about 1 atmosphere (100

pascals) at temperatures of 50-60C over their melting points. High vapor pressures may cause problems with ampoule ruptures and can also cause vapor transfer of material in the ampoule, which affects the amount of segregation that can be achieved. To reduce the vapor transfer of material during zone refining, a heater wire was wound around the outside of the ampoule, as shown in **Figure 1**. The zone refiner has four ring heater zones that can achieve 600C. The junction of the type-K thermocouple (plug visible on the top rail of the zone refiner), is placed on the inside surface of one of the ring heaters and is used to monitor the temperature. The temperature controller for the ring heaters is run in manual mode to reduce thermal fluctuations due to convection and small movements of the thermocouple (TC) junction relative to the heater. The heater wire is powered with a Variac and when current is passed through the heater wire, the gradient between the ring heaters and the unheated gaps is reduced, which reduces the amount of condensed material on the top of the ampoule between the ring heaters. The zones were translated at 5 cm/hr and 95 full length passes were run per ampoule. This is undoubtedly more passes than is required, but the process was automated and little additional effort was required to ensure maximum segregation was achieved.

Table I – Physical properties of Cd, Zn and Te for zone refining

	Thermal Conductivity K (W/m-K)	Melting Point (C)	Vapor Pressure (pascals)	V. P. Temp. (C)	Degrees over M.P.
Cadmium	97	321	100	381	60
Zinc	120	420	100	477	57
Tellurium	3	450	100	502	52

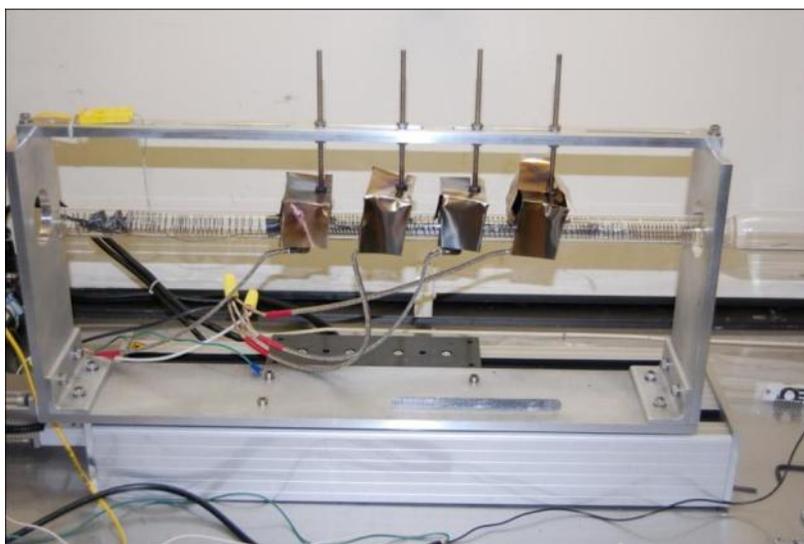


Figure 1 Zone refiner for purifying Cd, Zn and Te. Four ring heaters with stainless steel reflectors and a type-K TC are attached to the top rail and the translation stage is on the bottom.

Glow discharge mass spectroscopy (GDMS) results for 13 impurities in zone refined Te are shown in **Table II**. A 74 element scan was done, but the other elements were below detection limits or used in the measurement (Ta, In). All four ring heaters were used for Tellurium refining, due to its low thermal conductivity. It is seen that Se and metallic impurities Fe, Ni, Cu and Zn segregate to the first to freeze end of the ampoule. Na, Mg and P are concentrated in the middle of the ampoule and Cl and especially Oxygen were concentrated in the last to freeze part of the ampoule. GDMS is not effective in measuring Oxygen concentration, but the surface oxide segregated to the last to freeze end of the ampoule.

Cadmium was zone refined with only two ring heaters, due to its higher thermal conductivity, and the Cd ampoule was carbon coated to prevent the Cd from sticking to the ampoule. The top portion of the carbon coating was burned off to allow inspection of the melt zones during purification. GDMS results for Cadmium are still pending. Zinc has not yet been zone refined.

Table II – GDMS results in parts per million weight for Te zone refining

	First to freeze	Middle	Last to freeze
Element	Concentration	Concentration	Concentration
	[ppm wt]	[ppm wt]	[ppm wt]
Na	0.009	0.1	0.08
Mg	0.006	0.15	< 0.005
Al	0.21	0.13	0.13
Si	0.49	0.5	0.46
P	< 0.005	0.01	< 0.005
Cl	0.1	0.2	0.45
Ti	0.002	< 0.001	< 0.001
Cr	0.01	< 0.005	0.006
Fe	0.15	0.05	0.06
<i>Ni</i>	<i>0.09</i>	<i>< 0.005</i>	<i>< 0.005</i>
<i>Cu</i>	<i>0.61</i>	<i>0.04</i>	<i>0.01</i>
<i>Zn</i>	<i>1</i>	<i>0.02</i>	<i>0.05</i>
<i>Se</i>	<i>1.2</i>	<i>< 0.05</i>	<i>< 0.05</i>

2.2 Crystal growth

2.2.1 Synthesis

Immediately before loading for synthesis, the zoned material was removed from the ampoules and divided into quarters. The first to freeze and last to freeze quarters were discarded and the middle two quarters were used to synthesize the growth charge. The Cadmium was removed and etched with a 2:2:1 solution of acetic acid, hydrogen peroxide and nitric acid, rinsed in methanol and dried with nitrogen gas. The Zinc was etched to size with 50% aqua regia in DI water and then a finishing etch with the 2:2:1 solution was used. The Te was used without further processing from the ampoule, with a small portion crushed to attain the correct stoichiometry. A carbon coated synthesis tube was loaded with stoichiometric portions of the Cd, Zn and Te with an extra 0.5% of Tellurium.

The synthesis tube was sealed under vacuum and loaded into the Mellen rocking furnace shown in **Figure 2**. The tube was loaded in a nearly horizontal orientation to help disperse heat and to prevent plugging and rupture as the elements melt, react and solidify into the higher melting binary compounds. The furnace temperature was ramped up at 60C/hr until 10 degrees below the melting points of the elements and the binary compounds. In a range from minus 10C to plus 10C from each melting point, the ramp rate was 10C/hr to allow heat from the highly exothermic reactions to dissipate. At 1120C, the furnace was rotated between horizontal positions to completely homogenize the melt. After 6 hours of mixing, the melt was quenched to solidify the homogeneous charge.



Figure 2 Mellen rocking furnace for synthesizing the homogeneous CZT growth charge

2.2.2 Growth

Four crystals have been grown in the 24-zone PMZF Bridgman crystal growth furnace (**Figure 3**), which was designed and built at Northrop Grumman, in Bethpage, NY. All four crystals have been grown in carbon coated quartz ampoules (ID=38mm) with a 1C/mm gradient at a translation rate of 0.42mm/hour (10 mm/day). The details of the four growth experiments and the plan for CZT-5 are listed below:

1. Baseline unseeded growth with as-received 6N material, charge = 960g
2. Seeded growth with as-received 6N material, charge = 519g
3. Choked seeded growth with tapered ampoule and zone refined Te, charge = 456g
4. Unseeded growth with zone refined Te and new PMZF power supply, charge = 437g
5. Choked seeded growth with tapered ampoule and zone refined Cd and Te, charge = 424g

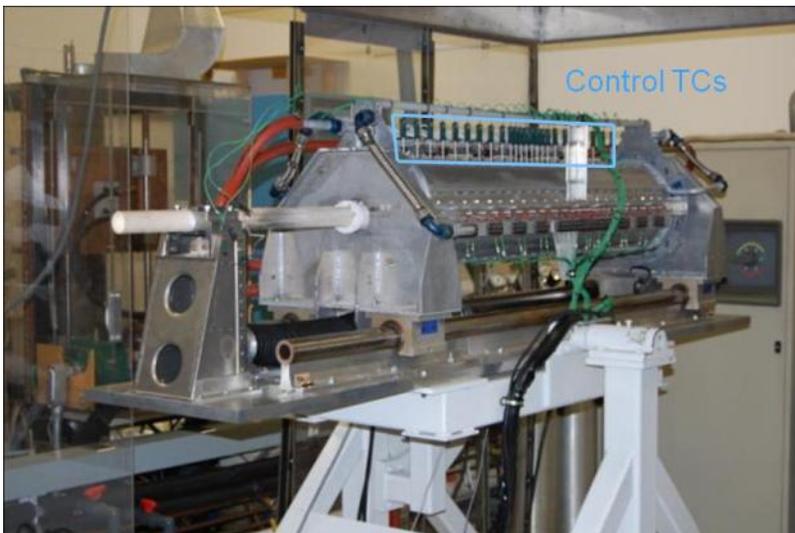


Figure 3 PMZF Bridgman crystal growth furnace, in horizontal orientation for ampoule loading

Four representative wafers (as-cut with a wire saw) from CZT-1 are shown in **Figure 4**. This was an unseeded growth using as-received 6N material from 5N Plus. The grain boundaries are located by observing different light reflections from a directional light source and are then marked with a pen. The straight lines are twin boundaries. Wafer 1 is the first wafer cut above the cone shoulder and wafer (-1) is the first wafer cut below the cone shoulder. There are some cutting and cleavage features on the right side of these wafers. There are multiple grains in wafer 1, with twins present in the top half of the wafer. By wafer 5, the twins have grown out of the large grain on top, leaving single crystal CZT. Unfortunately, extra grains nucleate and grow into the top right side of wafer 7, but by wafer 14, two large grains dominate the wafer with twin boundaries in the larger grain.

Figure 5 shows a plot of temperature (left y-axis) and duty cycle (right y-axis) for three representative heater zones in the PMZF over a five day period. The PMZF generally achieves control of $\pm 0.1\text{C}$ in each zone, but a 0.5C excursion can be seen in the graph at about 0.9 days past the start of the graph, which may cause extraneous nucleation. The duty cycle (or the PID calculated power required for steady temperature) is generally smooth, with a fast (barely visible) spike at the 0.5C excursion and other slower changes visible. Heater zone temperatures can be kept relatively steady when the power required in a zone changes at slow rates. Detectors were cut and fabricated from this crystal and evaluated. The results will be discussed in Section 3.

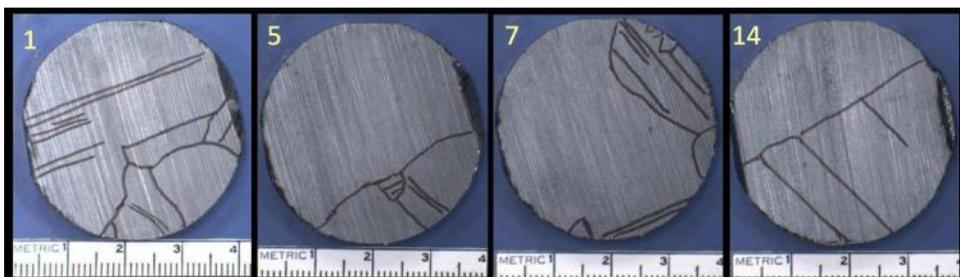


Figure 4 Wafers 1, 5, 7 and 14 from CZT-1. Grain boundaries are marked with pen and straight lines are twin boundaries

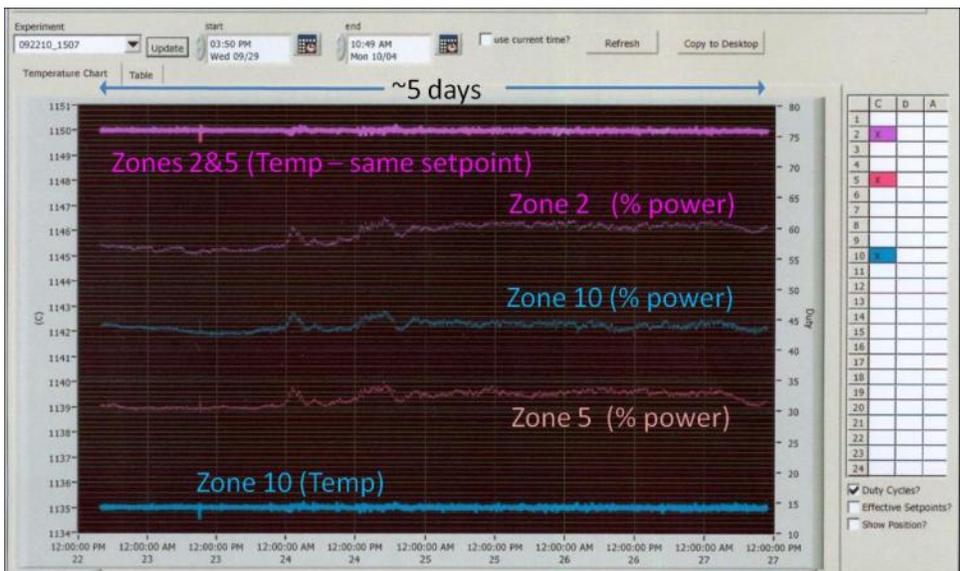


Figure 5 Plot of temperature and power duty cycles for three heater zones during CZT-1. The x-axis spans five days, with axis labels every twelve hours. The 0.5C control upset is just before one day elapsed in this graph

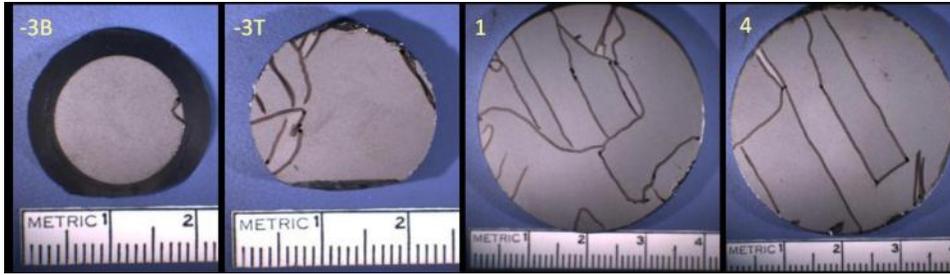


Figure 6 Wafers (-3) bottom view, (-3) top view, 1 and 4 from CZT-2 after lapping

Figure 6 shows bottom and top views of wafer (-3), wafer 1 and wafer 4 from CZT-2, which was a seeded growth. It can be seen from the bottom view of wafer (-3) that seeding resulted in a nearly single crystal in the lower cone of the ampoule, but one small grain from the bottom of the wafer has developed into two or three larger grains on the top of wafer (-3). Wafer 1 has several grains with twins, but the crystallinity improves by wafer 4, with fewer and larger grains present. The thermal control in heater zones 2, 5 and 10 is shown in **Figure 7**, with large upsets in duty cycle circled. This upset resulted in 0.5C temperature changes on thermocouples attached to the ampoule. This must be due to instability in the furnace control/power system, since normal control fluctuations would not result in duty cycle changes of 5-10 percent. The behavior in the thermal control generally correlates with the crystallinity shown in CZT-2, with good crystallinity during the initial phase followed by extraneous nucleation during the control upset and finally followed by improved crystallinity at the end of the ingot before the second thermal upset.

After this growth, the thermocouple A/D boards that had been a previous source of poor control on the PMZF were replaced and a calibration experiment was run, with the furnace operating normally.



Figure 7 Temperature control in selected heater zones during CZT-2, with two upsets in duty cycle circled

The third growth was grown with the choked seeding technique using Tellurium that had been zone refined and as-received Cd and Zn. A schematic for the choked seeding ampoule is shown in **Figure 8**, with a capillary connecting the seed pocket and the cone of the ampoule, which is meant to decrease subgrains in the ingot. In addition, there is a small

taper of approximately 1 degree that is designed to reduce stress in the crystal during the growth process. Unfortunately, the third growth had very poor crystallinity, with voids and large Te inclusions throughout, as can be seen in two typical wafers in **Figure 9**.

The unstable thermal control during CZT-3 is shown in **Figure 10**. The entire growth was marked by unstable temperature control and there were regular 0.5C degree fluctuations in the control TCs and ampoule TCs. The most likely remaining cause of the instability was a failing power supply, which was replaced.

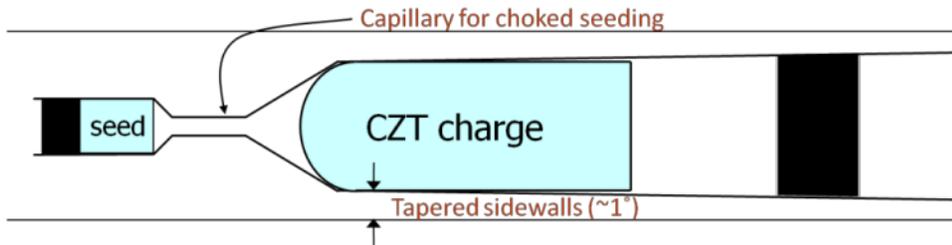


Figure 8 Choked seeding ampoule with tapered sidewalls

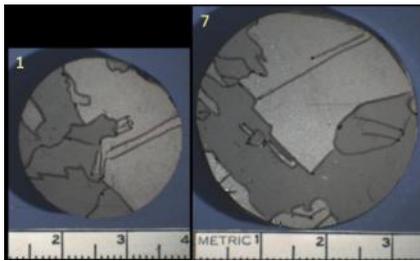


Figure 9 Wafers 1 and 7 from CZT-3, using the choked seeding technique with unstable power supply



Figure 10 Unstable temperature control during CZT-3 after thermocouple A/D board replacement

CZT-4 was an unseeded growth using zone refined Te and as-received Cd and Zn, and was the first growth with the new solid state power supply. Like CZT-1, the growth ampoule had a 5mmx5mmx25mm seed pocket that should provide some grain selection before the ampoule cone. As shown in **Figure 11**, there are several grains visible in wafer 2. There are two twin boundary structures in the top left hand of wafer 2 that are moving to the bottom, right side of wafers 3 and 4 as the growth progresses, leaving a large single crystal grain in the top left hand side of wafer 4. Unfortunately, there was a failure in the building's water cooling loop during CZT-4 and the cooling water for the furnace had to be manually switched to city water during the middle of the growth cycle, which caused a one to three degree C disturbance in the heater zones and an 8 degree disturbance on ampoule TC#5, which can be seen in **Figure 12**. This appears to be the likely cause of the two small grains circled in wafer 5, since it is unusual for grains to be nucleated in the middle of a large grain without a large temperature fluctuation at the melt-solid interface. The crystallinity of the wafers after wafer 5 grew worse, due to the new grains. The superimposed spike from ampoule TC#5 was plotted at 50% scale to fit on the graph. Ampoule TC#5 measured approximately 1080C during the upset and was located on the outer ampoule wall, near the furnace wall. As a result, despite the excellent thermal stability shown in **Figure 12**, CZT-4 had disappointing crystallinity.

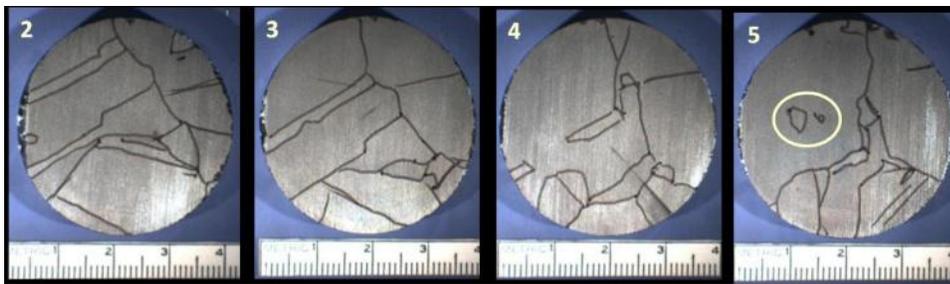


Figure 11 Selected wafers from CZT-4 grown with a new power supply

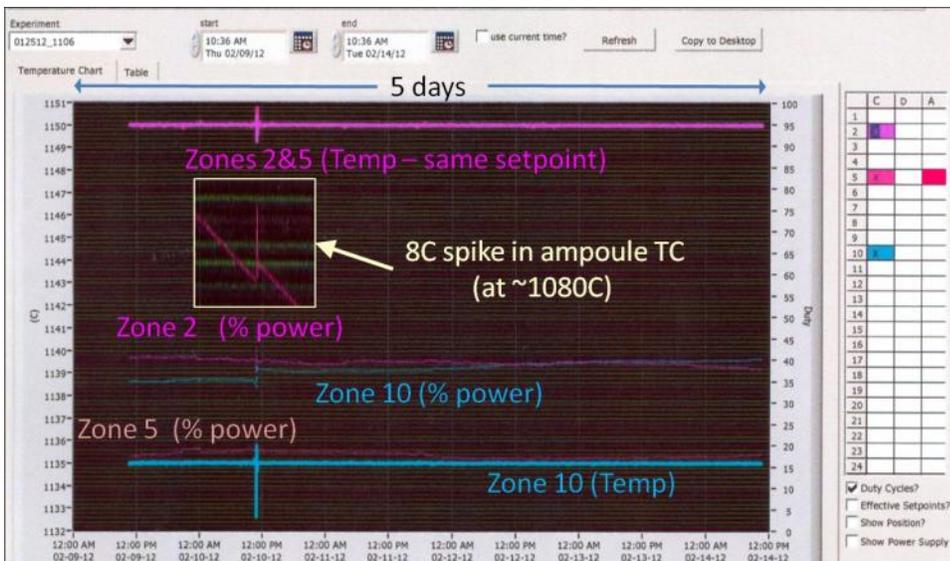


Figure 12 Thermal control during CZT-4 after the new power supply was installed. The temperature spike in ampoule TC#5 (~1080C) during the cooling water switch is superimposed at 50% scale for comparison to the heater zone spikes.

The next growth (CZT-5) will be a choked seeded growth using zone refined Cd and Te and as-received Zn. The new solid state power supply should enable superior thermal control, as shown in **Figure 12**. In addition, a switch has been

installed in the cooling water loop, so any interruptions in cooling water will result in an automatic switch to city water cooling.

3. RESULTS AND DISCUSSION

As shown above, the growth results have not been as good as hoped for. The best crystallinity was obtained in CZT-1, which was a 960 gram, unseeded growth. Although unseeded, there was a large period of stable thermal control during this growth and the grain size improved toward the end of the growth. Wafers from CZT-1 were cut and polished and sent to Brookhaven National Lab (BNL) for characterization. As shown in **Figures 13** and **14**, the FWHM of the energy resolution was 10% and the mu-tau product was $1.1 \times 10^{-3} \text{ cm}^2/\text{V}$. The resistivity was $3.5 \times 10^{10} \text{ Ohm-cm}$ and no hole transport was measured at a bias of 500V for a 3mm thick sample. These are reasonable, but not state of the art values and it was assumed that subsequent improved crystallinity from the choked seeding technique and decreased deep level trapping obtained by using zone refined raw materials would improve these values.

No measurements were taken for CZT-2 and CZT-3, due to the poor crystallinity caused by poor thermal control during growth. Three wafers from CZT-4 are currently at BNL for characterization. The plan for CZT-5 is to combine choked seeding with zone refined Cd and Te and will utilize the improved thermal control provided by the new power supply. In addition, an automatic switch has been installed in the cooling water loop to prevent future temperature spikes in the event of another cooling water failure.

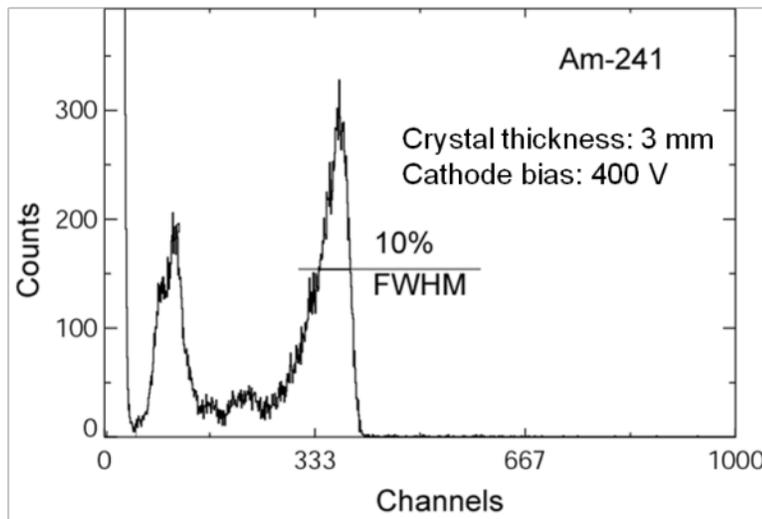


Figure 13 Energy resolution measured for CZT-1 on a 3 mm thick sample at 400V with an Am-241 source

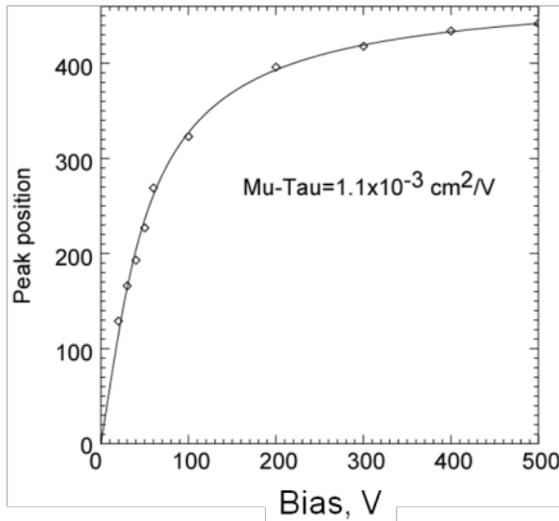


Figure 14 Mu-tau product measured for CZT-1 by fitting the Hecht equation

4. CONCLUSIONS

Detector grade CZT was produced using as-received 6N material from 5N Plus, Inc. without seeding. Successful seeding was achieved in CZT-2, but the subsequent crystal growth was degraded by poor temperature control and no characterization was done for CZT-2. CZT-3 was grown with choked seeding and zone refined Te, but the results of the choked seeding and purification cannot be evaluated, due to very poor crystal quality caused by the unstable power supply for the PMZF. The power supply was replaced before CZT-4 (unseeded with purified Te) and performed well, but crystallinity seems to have suffered when the cooling water for the furnace was switched to city water, causing a large temperature spike. Three wafers from CZT-4 are currently at BNL for characterization. CZT-5 will contain purified Cd and Te and use the choked seeding technique. The new power supply should continue to provide excellent thermal control and a switch has been installed in the cooling water loop to automatically switch to city water, in the event of another cooling water supply failure. It is expected that these precautions will allow an evaluation of the effectiveness of the combination of choked seeding with purified raw materials to improve radiation detection properties of CZT.

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