Abstract—The growth of large-volume semi-insulating CdZnTe single crystals with improved structural perfection has been demonstrated by the electro-dynamic gradient (EDG) technique and active control of the Cd partial pressure in the ampoule. The EDG furnace nearly completely eliminates the uncontrolled radiative heat transport commonly encountered in traditional Bridgman systems where the charge and furnace move relative to each other. Since the new furnace utilizes electronically controlled high-precision gradient translation it achieves superior thermal stability throughout the growth. The control of the Cd partial pressure allowed the solidification and cool-down of the ingots close to the stoichiometric composition. As a result, the formation and incorporation of large size (≥ 1 μm diameter) Te inclusions was avoided during crystallization and ingots with high structural perfection were achieved. Adequate electrical compensation has been achieved in most of the crystal growth experiments yielding CdZnTe crystals with bulk electrical resistivity in the $10^9 - 10^{10}$ Ωcm range and electron mobility-lifetime product as high as $\mu \tau_e = 1.2 \times 10^{-3}$ cm$^2$/V. The materials exhibit good spectral performance in the parallel plate detector configuration.

I. INTRODUCTION

The industrial scale growth of semi-insulating Cd$_{1-x}$Zn$_x$Te (0 ≤ x ≤ 0.2) for room-temperature x-ray and gamma-ray radiation detector applications has been hampered by low yields of large-volume single crystals with uniform charge transport properties. All of the crystal growth techniques employed today such as the traveling heater method, conventional Bridgman, high-pressure Bridgman and gradient freeze techniques are essentially producing large-grain polycrystalline ingots [1]-[5]. Although, all of these techniques have occasionally yielded single crystal CdZnTe ingots up to 50 mm diameter they yet to demonstrate the stable and reproducible growth of single crystal ingots on the industrial scale with diameter 100 mm and more. Much of these difficulties are related to the inherent thermo-physical properties of CdZnTe at temperatures close to the melting point and the resulting uncontrolled formation and evolution of lattice defects during crystallization and the subsequent cool-down of the ingots. Advancement of the crystal growth systems and much improved control over heat transport both in the melt and the solid are needed to achieve better control over the defect formation and evolution during the CdZnTe crystal growth process. Here we report on the development of a crystal growth system designed to reduce defect formation and improve the crystalline perfection of radiation detector grade CdZnTe ingots. The new electro-dynamic gradient (EDG) furnace is based on our research on the gradient freeze growth technique. The new furnace nearly completely eliminates the problems resulting from uncontrolled radiative heat transport commonly encountered in traditional Bridgman systems where the charge and furnace move relative to each other. Since the new furnace utilizes electronically controlled gradient transport they achieves superior thermal stability throughout the growth. The new conventional EDG furnace allows high precision translation of the temperature gradient and precise control of the Cd partial pressure in the ampoule during the crystal growth.

II. CRystal GROWTH CHALLENGES

The growth of semi-insulating (SI) CdZnTe crystals, with spatially uniform charge transport properties required by radiation detector applications, poses a considerable challenge for crystal growers. In addition to the difficulties of growing large-volume, uniform single crystals with low dislocation, precipitate and inclusion density, the stringent requirements for tuned electrical transport properties add additional challenges. The need to maintain a very low net free-carrier density ($10^5 - 10^6$ cm$^{-3}$), and low density of carrier traps and recombination centers requires very good control over the purity and the stoichiometry of the material.

The fundamental material science challenges of CdZnTe crystal growth can be divided into three categories: A) charge transport properties, B) single crystal volume, and C) single crystal uniformity.

A. Charge Transport Properties

Radiation detector applications require sensor materials with high electrical resistivity and long lifetime...
(recombination and trapping) of the charge carriers. To achieve the maximum resistivity allowed by the band gap of the material, and sufficiently low defect concentrations for reasonably long carrier lifetimes, careful control of the incorporation of electrically active defects is required during the crystal growth of semi-insulating CdZnTe.

It is now widely accepted that complete electrical compensation in SI CdZnTe is achieved by localized defects with deep electronic levels close to the middle of the band gap, as discussed by Neumark in her seminal paper [7]. Unfortunately, the same deep level defects that assure the electrical compensation and high resistivity of the CdZnTe crystals also serve as recombination centers and carrier traps and seriously deteriorate the charge transport in the material. Based on the measured electron, $\tau_e = 10^{-6}$ s, and hole lifetimes, $\tau_h = 10^{-7}$ s, and the published capture cross sections of deep levels [8], one can estimate the density of electron ($N_e$) and hole ($N_h$) traps in SI CdZnTe. Today the typical values are about $N_e = 10^{14}$ cm$^{-3}$ and $N_h = 10^{15}$ cm$^{-3}$, respectively. As a rule of thumb, an order of magnitude increase of the carrier lifetimes would require an order of magnitude reduction of the density of the corresponding carrier traps.

B. Single Crystal Volume

Except for a few experimental programs, at present almost all of CdZnTe single crystal growth is performed with a variant of the directional solidification technique. In these techniques, (Bridgman, gradient freeze, traveling heater method) a temperature gradient is passed through the melt to obtain large single crystals. The probability of obtaining large single crystals depends on the physical properties of the material in the liquid and solid phase and the thermal properties of the crystal growth equipment. Single crystal growth is therefore a thermodynamic and heat transport problem. The progress of the solidification is the function of the heat flow at the solid-liquid interface.

$$\Phi_s = \rho_s H_f R + \Phi_l$$  \hspace{1cm} (1)

where $\Phi_s$ and $\Phi_l$ are the heat flux in the solid and the liquid, $\rho_s$ is the density of the solid, $H_f$ is the heat of fusion and $R$ is the growth rate. In the approximation that heat is primarily transported by thermal conduction at the solid-liquid interface, the heat balance equation simplifies to

$$k_s G_s = \rho_s H_f R + k_l G_l$$  \hspace{1cm} (2)

where $k_s$ and $k_l$ are the thermal conductivity of the solid and the liquid, and $G_s$ and $G_l$ are the temperature gradients in the solid and liquid, respectively. The above equation shows that the solid has to transport the heat from the melt and the heat released during solidification (the solidification of CdZnTe being an exothermic reaction). The low thermal conductivity of solid CdZnTe poses a significant challenge to maintaining the heat flow balance at the interface and dictates the use of slow growth rates and relatively large temperature gradients to grow large single crystals. A realistic description of the heat transport in real crystal growth systems is a complex problem that takes into account all the heat transport modes (conductive, convective and radiative) in the melt and solid, growth crucible and furnace. This can only be accomplished by numerical modeling of the crystallization process. An example of thermal modeling for a multi-zone vertical EDG system is shown in Fig. 1.

Besides the adequately designed heat flow, the thermal stability of the crystal growth system is the most critical factor for successful single crystal growth. Temperature fluctuations and thermal drift of the growth furnace can cause uncontrolled changes of the shape of the growth interface and induce spurious nucleation. In a classical Bridgman growth, where the charge and the furnace move relative to each other, it is difficult to achieve adequate long-term stability of the growth interface, as the radiative heat transport continuously changes at the ends of the growth crucible with the progress of the translation (Fig. 2a). Such effects can be eliminated, and the heat-transport control stabilized, in the gradient freeze technique where the growth crucible and the heater are stationary and the translation of the temperature gradient is achieved by programmed lowering of the temperature set-points in a multi-zone furnace (Fig. 2b). The disadvantage of the gradient freeze technique is the continuous change of the temperature gradient at the melt-solid interface as the solidification progresses. As a result both the crystallization rate and the convection in the melt changes during crystal growth and need to be taken into consideration to obtain larger single crystals.

This effect can be eliminated if the translation of the temperature gradient zone is achieved electronically. This technique is called Elecro-Dynamic Gradient (EDG) growth in the literature. With state of the art temperature control
techniques versatile crystal growth systems with superior thermal stability can be designed and constructed today.

We have adopted the EDG technique for both the conventional and high-pressure growth systems. Results from the conventional vertical directional solidification of semi-insulating CdZnTe using an advanced EDG furnace with Cd partial pressure control will be discussed in this article.

C. Single Crystal Uniformity

There are numerous structural defects that hamper the uniformity of CdZnTe single crystals such as dislocations, sub-grain boundaries, Te precipitates and Te inclusions. Many of these defects are associated with charge trapping and recombination, and were found to adversely affect charge transport. Recently it was shown that dislocations introduced by deformation in CdZnTe are associated with a localized defect level with ionization energy of 0.27 eV [9]. Significant concentration of dislocations is typically introduced during the growth process of the CdZnTe crystals, due to the thermal stress during solidification and cooldown. Dislocations intersecting a polished surface of a <111> oriented CdZnTe crystal can be revealed by appropriate defect etching [10]. Fig. 3 shows dislocation-related etch pits for a CdZnTe single crystal with a very high dislocation density. In this case, cellular arrangements of the etch pits are observed. Such a structure is typically observed if the crystal is grown in a high temperature gradient where the dislocations introduced undergo polygonalization, and form lower energy cellular structures or sub-grain boundaries. Charge trapping and recombination along the sub-grain boundaries is expected to produce non-uniform charge transport and poor performance of radiation detectors fabricated from such materials.

Almost all of the detector-grade CdZnTe produced today is grown from Te rich melts and the resulting ingots contain large concentrations of Te inclusions and precipitates. Here, we use the definitions of Rudolph and Mühlig for

Fig. 2. Comparison of the classical vertical Bridgman a) and the gradient freeze crystal growth technique b). $T_m$ is the melting point and the horizontal dashed lines show the progress of the solid-liquid interface. In the Electro-Dynamic Gradient (EDG) system the gradient motion is achieved electronically (as in a)) without moving the furnace or crucible relative to each other.

Fig. 3. Cellular arrangements of etch pits or sub-grain boundaries (dark spots) in a (111) oriented CdZnTe crystal containing large density of dislocations.

Fig. 4. IR image of randomly distributed Te inclusions in a CdZnTe single crystal.
inclusions and precipitates [11]. Precipitates are formed during the cooling process and originate from the retrograde slope of the solidus line [12]. The nucleation and growth of Te precipitates is controlled by atomic diffusion. The average diameter of Te precipitates is 10 – 30 nm. In contrast, the typical diameter of Te-rich inclusions formed in CdZnTe is in the 1 – 50 µm range. Inclusions originate from morphological instabilities at the growth interface, as Te-rich melt droplets are captured from the boundary layer ahead of the interface. Fig. 4 shows an infrared (IR) microscopy image of a typical CdZnTe slice showing Te inclusions as dark spots. Fig. 5 shows a transmission electron microscopy (TEM) image of a triangular Te inclusion. Inclusions are typically surrounded by a dense field of dislocations as seen in the x-ray topography image in Fig. 6. Isothermal annealing of CdZnTe in Cd vapors can dissolve Te inclusions; however, the dislocation field surrounding the inclusion stays behind. Te inclusions formed at the growth interface, and embedded into single crystal grains, can migrate during the cool-down of the CdZnTe ingot under the influence of the temperature gradients existing in the ingot (thermo-migration) [13]. This process can be understood as the dissolution of the CdZnTe by the Te melt at the high temperature side of the inclusion and the re-crystallization of the CdZnTe matrix at the cold end of the inclusion [14]. Upon arriving at structural defects such as grain boundaries, twin boundaries and sub-grain boundaries, the Te inclusions get pinned, hindering their further migration. Such a process can explain the often-observed decoration of large defects in CdZnTe grown from Te rich melts.

Te inclusions, and the dislocation fields associated with them, are expected to adversely affect charge transport in nuclear radiation detectors fabricated from CdZnTe single crystals. In particular, non-uniform distribution of Te inclusions likely causes a severe deterioration of the performance of the devices. It is well documented that correlated arrangements of Te inclusions such as decorated grain boundaries, cause severe deterioration of charge transport due to charge trapping at these defects and the distortion of the internal electric field distribution. As a result, detectors fabricated from polycrystalline CdZnTe show poor performance compared to single crystal devices. The material non-uniformity leads to a point-by-point spatial variation of the charge transport through the device and results in a severe deterioration of the energy resolution and efficiency of the device. Since most of the studies were performed on CdZnTe polycrystals with decorated structural defects, it is unclear at this point what the effect of un-decorated grain boundaries, twins and sub-grain boundaries is on the charge transport properties in CdZnTe. Recently, it was shown that non-uniform distribution of Te inclusions also deteriorates the spectroscopic performance of large-volume single-crystal CdZnTe detectors. It was also shown from a geometric argument that the region of degraded charge transport near the Te inclusions extends beyond the volume of the inclusion itself [15].

Te inclusions can be eliminated from CdZnTe crystals by controlling the Cd partial pressure during crystal growth [13], [16]. The suppression of the Te inclusion formation during crystal growth by controlling the melt composition offers several benefits over post-growth annealing of SI CdZnTe.

![Fig. 5. TEM image of a triangular shaped Te inclusion in CdZnTe.](image)

![Fig. 6. X-ray topography image of the dislocation field surrounding a Te inclusion in CdZnTe.](image)

When the formation of Te inclusions is suppressed, the associated dislocation fields are eliminated as well. Impurities usually trapped at Te inclusions are segregated at the first-to-freeze and last-to-freeze section of the ingots. It is anticipated that with this approach CdZnTe single crystals with more uniform charge transport properties can be grown for nuclear detector applications.

In this paper, we present and discuss experimental results for the growth of CdZnTe single crystals free of Te inclusions grown with the EDG and the vertical gradient freeze technique employing Cd partial pressure control.
III. EXPERIMENTAL RESULTS

A. Crystal growth experiments

We performed a series of crystal growth experiments in two different advanced multi-zone EDG furnace using Cd partial pressure control. The geometry of the furnace/ampoule assembly and a typical gradient freeze temperature program is illustrated in Fig. 7 for one of the furnaces. The crucible/ampoule assembly with the Cd reservoir is shown in Fig. 8. We used high-purity silica tubes to prepare the ampoules and glassy carbon crucibles to grow the Cd$_{1-x}$Zn$_x$Te ($x = 0.1$) ingots. 6N purity Cd, Zn and Te were used to synthesize the CdZnTe compound. The charge was placed into a silica ampoule with an extension for a Cd reservoir that was evacuated to $\leq 2 \times 10^{-7}$ torr and sealed under vacuum. The growth was performed using the EDG technique i.e. translating the temperature gradient through the melt electronically. We used low temperature gradients and low growth rates to minimize thermal stress and produce material with low dislocation density and to avoid constitutional supercooling effects. The Cd reservoir temperature was varied between 800°C and 850°C in these experiments to achieve various melt stoichiometry during crystallization. The temperature of the Cd reservoir was programmed throughout the solidification and cool-down in such a way to maintain the desired stoichiometry of the CdZnTe melt and solid.

Fig. 9 shows a 92 mm diameter 4 kg CdZnTe ingot grown by the vertical EDG technique using Cd partial pressure control. 95% of the ingot is one large single crystal. A number of twins are observed throughout the crystal as seen in Fig. 10 that shows a radial slice form the ingot. The one dominant large single crystal grain clearly demonstrates the excellent thermal stability of the EDG furnace. The presence of twins suggests that excessive stresses persisted during solidification of the ingot. The elimination of the twins will require further optimization of the heat-flow pattern of the EDG furnace and refinement of the crystal growth program.

![Fig. 7. Vertical Bridgman furnace and gradient freeze temperature program used in some of the CdZnTe crystal growth](image7.png)

![Fig. 8. The crystal growth ampoule and Cd reservoir configuration.](image8.png)
B. Stoichiometry control

We have performed a set of experiments to suppress Te inclusion formation in CdZnTe crystals. For this purpose we have varied the starting composition of the melt as well as the ratio of the melt temperature and the Cd reservoir temperature during solidification. Fig. 11 illustrates the results in a set of infrared (IR) microscopy images taken on 12 – 30 mm thick slices of 50 mm diameter CdZnTe ingots grown under various stoichiometry conditions. Under poor stoichiometry control conditions large density of Te inclusions are formed during solidifications both inside single crystal grains and along structural defects such as grain boundaries, twins and sub-grain boundaries. For the ingot grown with favorable stoichiometry conditions no Te inclusions are visible with diameter larger than 1 µm (the resolving power of IR microscopes).

Fig. 9. 92 mm diameter 4kg SI CdZnTe ingot grown by the EDG technique and Cd partial pressure control.

C. Charge transport properties

To study the charge transport properties of the CdZnTe crystals grown with the vertical EDG or gradient freeze techniques and Cd partial pressure control, 5×5×2 mm³ single crystal samples were fabricated from radial slices cut close to the first-to-freeze (tip) and last-to-freeze (heel) section of the ingot. The samples were etched in dilute Br - methanol solution to remove the surface damage introduced during cutting. Platinum electrodes were deposited by sputtering the 5×5 mm² area surfaces of the crystals, to form parallel plate detector structures. Current-voltage (I-V) measurements were performed to estimate the bulk electrical resistivity of the material. Examination of the I-V curves at low bias voltages showed the back-to-back Schottky junction characteristics typical for SI CdZnTe with Pt electrodes. The measured bulk resistivity of the CdZnTe crystals was in the $10^9 - 10^{10}$ Ωcm range.
The mobility lifetime product ($\mu_\tau$) of the charge carriers was determined from the bias dependence of the charge collection efficiency. To evaluate the collection efficiency, and estimate the $\mu_\tau$ values, the shift of the pulse height of the photopeak from the 5.5 MeV alpha particles from a $^{241}$Am source was measured as a function of the bias voltage and the resulting data fitted to the Hecht equation [17]. Electron mobility-lifetime product as high as $\mu_\tau_e = 1.2 \times 10^{-3}$ cm$^2$/V was obtained in some crystals. The hole mobility-lifetime product of the material was estimated to be less than $5 \times 10^{-5}$ cm$^2$/V.

Fig. 13 illustrates the detector performance of the CdZnTe crystals grown with the EDG technique and Cd partial pressure control. Such an excellent spectral performance is adequate for most of x-ray and gamma spectroscopy applications where sufficient detector efficiency can be achieved with 5 mm or thinner CdZnTe crystals.

IV. CONCLUSIONS

The growth of large-volume semi-insulating Cd$_{1-x}$Zn$_x$Te ($x = 0.1$) single crystals with improved structural perfection has been demonstrated by the electro-dynamic gradient (EDG) technique and active control of the Cd partial pressure in the ampoule. The crystal growth experiments were performed in EDG furnaces that nearly completely eliminate the problems resulting from uncontrolled radiative heat transport commonly encountered in traditional Bridgman systems where the charge and furnace move relative to each other. Since these new furnaces utilize electronically controlled gradient translation they achieve superior thermal stability throughout the growth. The control of the Cd partial pressure allowed the solidification and cool-down of the ingots close to the stoichiometric composition. As a result, the formation and incorporation of large size ($\geq 1$ $\mu$m diameter) Te inclusions was avoided during crystallization and ingots with high structural perfection were obtained. Adequate electrical compensation has been achieved in most of the crystal growth experiments, yielding bulk electrical resistivity of the CdZnTe crystals in the $10^9$ – $10^{10}$ $\Omega$cm range. The materials yielded detectors exhibiting good spectral performance in the parallel plate detector configuration and electron mobility-lifetime product as high as $\mu_\tau_e = 1.2 \times 10^{-3}$ cm$^2$/V.

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VI. REFERENCES


