



BNL-94031-2010-CP

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single crystals***

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*Presented at the 2010 SPIE Optics + Photonics Conference
San Diego, California
August 1 – 5, 2010*

August 2010

Nonproliferation and National Security Department

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Thermographic analyses of the growth of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ single crystals

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ABSTRACT

Bulk $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ ($0 < x < 0.1$) single crystals for gamma-ray detectors are grown mainly from near-stoichiometric melts. We discuss the influence of the thermal pre-history of the melts (superheating, thermo-cycling, and cooling rate) on various physical properties based on our thermographic analyses, electrical conductivity and viscosity measurements. Increasing the Zn content causes non-monotonic dependencies in the quality of the crystals' structure.

Keywords: CdZnTe detectors, structural transformations, phase transitions, Zn segregation

1. INTRODUCTION

The wide range of possible applications for $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ solid-solution single crystals, for example, in microelectronics, as substrates for $\text{Cd}_{1-y}\text{Hg}_y\text{Te}$, and in radiation detectors, constantly spurs studies of the various growth parameters that influence the crystal's structure. Previously, much attention was paid to exploring growth processes from the melts, the most promising method of producing large bulk crystals [1]. However, this method faces some critical physical- and chemical-problems that are difficult to control. The physical ones include convection in the liquid [2-4], variable liquid viscosity during growth [5], and differences in the thermal conductivity of the liquid- and solid-phases [6], so creating line defects, viz., dislocations and twins.

No less important are those related to the chemical peculiarities of the growth system. The process involves continuous material transfer between the three co-existing phases. Hence, the pressing demand for homogeneous material stimulated numerical investigations on the Cd-Zn-Te phase equilibrium with vapor, because Cd and Zn are volatile components; furthermore, notable ranges of homogeneity characterize both binary tellurides and the solid solution [7]. Observations showed that due to a noticeably wider $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ solidus in the Te side in comparison with the metal-component side, the ratio (Cd+Zn/Te) varies and deviates from stoichiometry [8]. Thus, the crystal grows under conditions that are far from equilibrium, thereby accounting for discrepancies in the literature about Zn segregation in solid-solution crystals grown from the melt [9].

Recently, the transition of $\text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}$ from the liquid to the solid phase was monitored *in situ* by eddy-current sensor techniques [10, 11] and by laser ultrasound [12]. Exploring the dependence of supercooling the melt on its superheating [10, 11] indicated that raising the temperature stimulates an increase in supercooling. Furthermore, supercooling to about 20 K causes spontaneous crystallization.

The aim of our study was to detail the influence of the melt's thermal pre-history (superheating and cooling rate) on various physical properties, using radiometric analysis and two modified methods of differential thermal analysis (DTA). For controlling temperature changes during CdZnTe melting, holding the material at different constant temperatures, and detailing the post-crystallization processes of the bulk crystals' growth, we used a real-time derivative thermal analysis (DrTA) system. To regulate the effects of the solidification process on specimens of small mass, we employed a digital differential thermal analysis (DgDTA) instrument.

2. EXPERIMENTAL TECHNIQUES

Bulk $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ ($0 < x < 0.1$) single crystals ($\varnothing 75$) mm were grown by the vertical Bridgman growth method in evacuated (to 10^{-3}) Pa quartz ampoules with covered with pyrolytic graphite walls. The composition of the starting

mixture of pure (6N) components was near stoichiometric. The ampoule was lowered at rates of 1-10 mm/h. During the experiments, a control thermocouple was fixed at the center of the ampoule's flat bottom. A computer assured the *in situ* DrTA control of thermal effects in the melt accompanying the structural transformations as the ampoule was lowered in a temperature gradient, and then held at the melt isothermal temperature. The control thermocouple was sampled at a frequency of 1-10 s⁻¹. Data from the control Pt/PtRh thermocouple (with accuracy ± 0,5 K) were processed automatically by calculating the derivative $dT/d\tau$ (where T is temperature, and τ is time). We estimated that the accuracy of temperature stabilization in the furnace in the area of isothermal holding was ± 0.5 K.

DgDTA was used to control the processes of melting and solidification of a 2g specimen at a rate of $V_c = 0.5\text{--}10$ K/min. The accuracy of the controlling Pt/PtRh thermocouple was ± 0.5 K.

We assessed the Zn segregation (k_{ZnTe}) in $Cd_{1-x}Zn_xTe$ crystals with $x=0.02, 0.04, \text{ and } 0.05$, using the Zn^{65} radioactive isotope (p^+, γ -radiation, $T_{1/2} = 245$ days). The solid-solution crystals were grown by the directional crystallization method in graphitized quartz ampoules. We employed a lowering rate of 6 mm/hour, and a temperature gradient at the crystallization front of 6 K/cm.

3. RESULTS AND DISCUSSION

Usually, bulk single crystals are grown from a pre-compounded solid charge that is overheated above its melting temperature. Thus, monitoring the melting processes can give information above the superheating range needed for full homogenization of the melt. Indeed, the findings from the DgDTA raised the possibility that the solid solution melts with an additional endothermic effect (AEE), similar to the binary compound CdTe [13, 14]. However, contrary to this compound, only one AEE was observed in the $Cd_{1-x}Zn_xTe$ melts ($0.02 < x < 0.1$), namely near 1392 ± 2 K. Figs.1-4 demonstrate that although the liquid phase appears at 1375 ± 2 K, small superheating above this temperature, even by approximately 20 K, does not assure full homogenization of the melts. Undoubtedly, certain small species are retained in the melt up to the AEE temperature that provokes their destruction. The tops of crystals grown from such melts contain many small grains, and hence, their upper parts became polycrystalline. Similar results were reported in [10] where holding the $Cd_{0.96}Zn_{0.04}Te$ melt for a long time, 24 h, at a low superheating temperature, ~1378 K, did not ensure the conditions for single-crystal growth. Fig. 1 clearly illustrates the reason for this fact; thus, “the low-temperature” holding provided conditions suitable for rapid spontaneous crystallization at a temperature noticeably higher than the melting temperature of the charge.

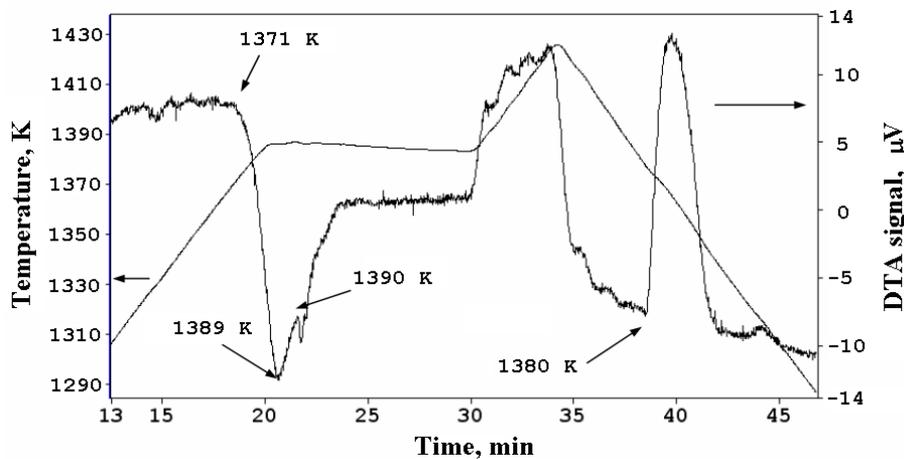


Fig. 1. DTA thermogram of melting, intermediate isothermal holding at 1390 K, and crystallization of the $Cd_{0.92}Zn_{0.08}Te$ sample ($V_{h/c} = 10$ K/min, $T_{melt,max} = 1425$ K).

As is evident from Figs. 2-4, holding the melt at a “high temperature”, in contrast can engender its supercooling. Accordingly, we must identify a compromise temperature at which to hold the melt before lowering the ampoule in the temperature gradient for directed crystallization.

Monitoring of the melt cooling process during the bulk crystal growth by analyzing the temperature vibrations in real time opened up the possibility of discovering the presence of a critical temperature at which periodic thermal

vibrations occur in the melts. Fig. 5 illustrates the sharp vacillations of the $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}$ melt temperatures when we lowered the ampoule at a rate of 1 mm/h after isothermal holding of it at 1401.5 K. The temperature oscillations in the range from 1394 -1379 K are so large that they were apparent in the growing system's temperature recording (the upper curve in Fig. 6). Comparing these data with the AEE temperature revealed by DgTA led us to conclude that the exothermic nucleation process begins at 1394 ± 2 K. Consequently, the appearance of oscillations is related both to melt composition and to the kinetic peculiarities of investigated systems' changes in thermodynamic parameters. The most probable cause of this phenomenon is the alteration of the melt structure at certain discrete temperature intervals.

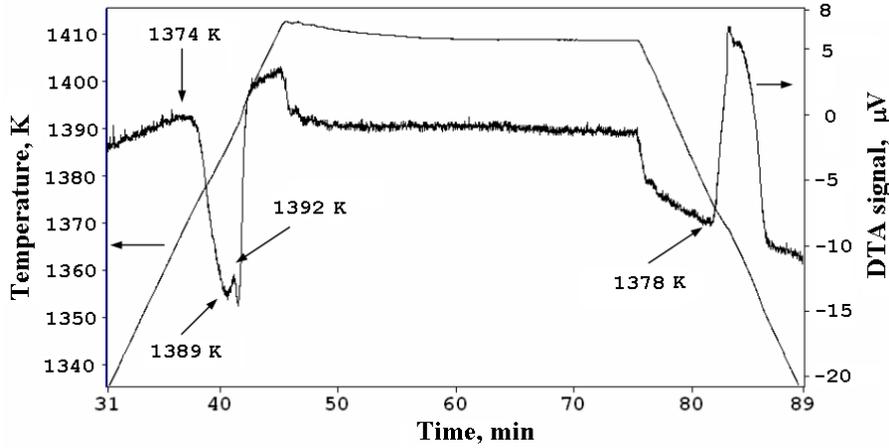


Fig. 2. DTA thermograms of melting, isothermal holding at 1410 K, and crystallization of the $\text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}$ sample ($V_{h/c} = 10$ K/min).

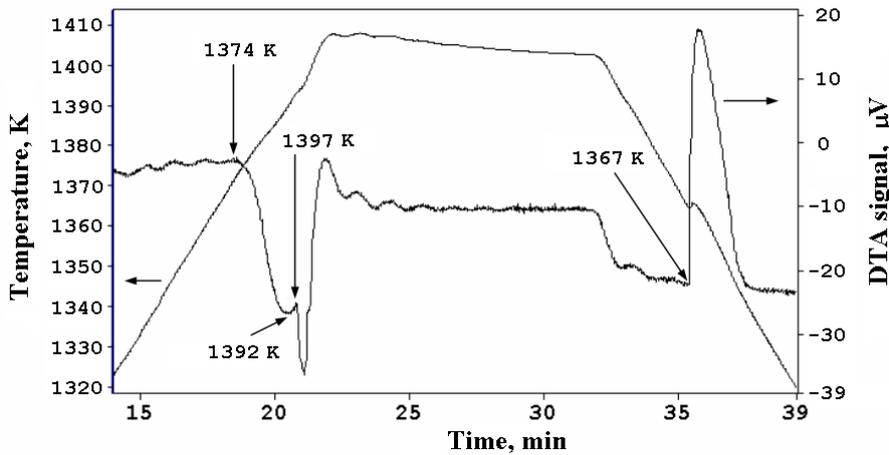


Fig. 3. DTA thermograms of melting, isothermal holding at 1405 K, and crystallization of the $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}$ sample ($V_{h/c} = 10$ K/min).

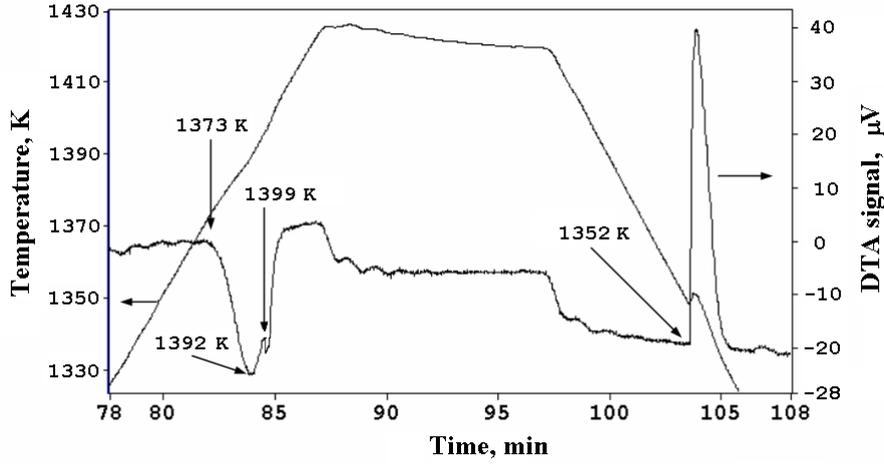


Fig. 4. DTA thermograms of melting, isothermal holding at 1420 K, and crystallization of the $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}$ sample ($V_{h/c} = 10 \text{ K/min}$).

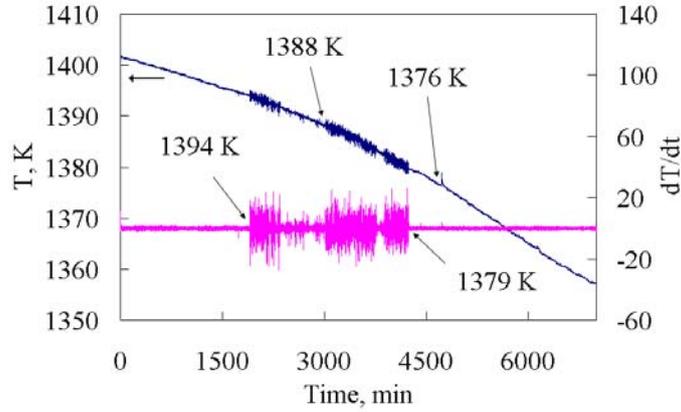


Fig. 5. The temperature oscillations of $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}$ melt during the directed crystallization from 1402 K at lowering speed of 1 mm/hour.

The phenomenon of the temperature instability in the melts of both metals and semiconductors long has been known, more frequently as the term “temperature above stable fluctuations” [15-17]. Usually, their nature is explained within the framework of the ideas of the melt-cluster theory. The inhomogeneity (fluctuations of the composition) of the melt, even in the case of an elementary metal, is a common property of a condensed system, demonstrating its accordance with the principle of the energy minimum. Undoubtedly, cluster sizes are a function of temperature: In the hotter part of the melt, they are fewer, and vice versa. In a temperature gradient, the clusters continuously exchange heat, so resulting in their irregularly changing disintegrations and associations. This heat absorption and emission is fixed by the thermocouple as thermal fluctuations. The amplitude of the melt’s thermal fluctuations depends on the degree of simultaneous enlargement or diminution of the clusters.

Fig. 6 illustrates Zn segregation in the crystals as a function of the crystallized melt fraction (g). The value of $k_{\text{ZnTe}} = 1.16$ is estimated via the Pfann equation:

$$C_s = C_0 k (1-g)^{k-1}, \quad (1)$$

where C_0 is the starting Zn impurity content in the melt, C_s is the Zn content in the g point, and g is the solidified part of ingot.

The Zn^{65} segregation dependencies in the solid solution, shown in this figure, generally represent crystallization regularities that are determined by the system’s phase diagram: ZnTe content decreases in the growth direction because

the solid solution, reached with the high melted component, crystallizes first. The results of Zn segregation, estimated by Eq. 1 with $k_{ZnTe}=1.16$ appear as the solid lines in Fig. 6.

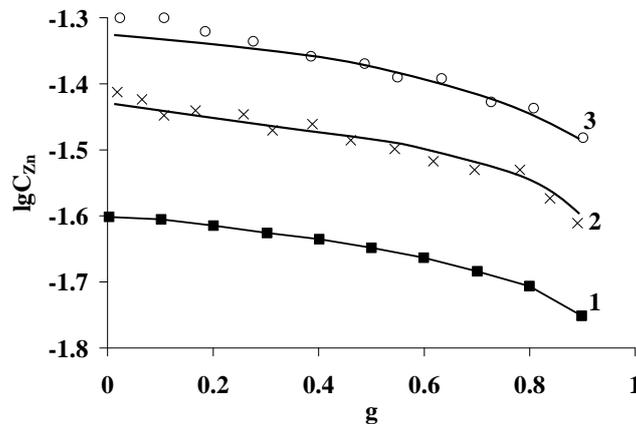


Fig. 6. Zn⁶⁵ composition along Cd_{1-x}Zn_xTe ingots, grown by the directed crystallization method ($\varnothing=75\text{mm}$) with $x=0.02$ (1); $x=0.04$ (2); $x=0.05$ (3).

As apparent from Fig. 6, the increased Zn content in the top of the ingots with $x \geq 0.04$ is larger than that theoretically calculated. The discrepancy between the calculated and experimental segregation is typical for most directional crystallization methods; it results from deriving the real growth condition from theoretical Pfann's equation. One of the main factors that will insure coincidence is the homogeneity of dopant concentration in the cross section. However, our autoradiographic analyses of the as-grown crystals showed irregular Zn segregation, not only along the crystal's axis, but in its cross-section too. Simultaneously, the distribution of inhomogeneities in the cross-section changes: Zn content in the first part of ingot increased from the center to periphery, but decreased in the end part of the ingot.

We also investigated the irregularity of the dopant's cross-sectional distribution by crystal lattice parameter a measurements. For this purpose, we employed a two-wave Bond and multi-wave diffractometry method with a relative error of $\Delta a/a \leq 10^{-5}$. Measurements of parameter a were taken on 15-20 plates with 3-mm thickness, with a (111) oriented surface. Our findings confirmed the results of our radiometric analysis of axial- and radial-ZnTe segregation. Segregation was most evident in the start and the end part of ingot; here, the radial changes of parameter a were centre-symmetrical and can be approximated by a parabolic equation. According to the X-ray analyses, the a values increased in the wafer from the side surface to its center by about 10-15 %, and decreased from 5-7 % in the end part of ingot.

Two effects might be responsible for the changes seen during the material's crystallization: The non-equilibrium of the crystallization process; and, Zn migration from the ingot's hot upper part to the cooler one during the cooling to room temperature. Inhomogeneity might be explained by effects of the deceleration of homogenization of the diffusion layer on the crystallization rate, the segregation-coefficient concentration dependence, and the other causes.

Our conclusion about the influence of the Zn diffusion influence on radial inhomogeneity of the solid solution's composition was grounded on our assuming that labeled dopant segregation on the grain boundaries took place only in the ingot's tip. It is uncertain whether these defects were present on the ingot's heel. Probably, a dopant, located in the lattice's interstitial position during long crystallization process, diffuses under the temperature gradient to the cooler parts of the crystal. Such an increase in the local concentration of Zn might lead to the reorganization of the defects by creating a more concentrated solid solution.

Indeed, an acceleration of the cooling process decreased the radial fluctuations in the crystal's composition. With the help of the radiometry method, we optimized the cooling regime for Cd_{0.96}Zn_{0.04}Te crystals. Thus, after completing the crystallization process, the ingot should be held for 1 hour on the plateau of the furnaces' lower-zone temperature profile to eliminate the excessive drop in the crystal's temperature. We established that temperature gradient along the ingot cannot be greater than 10-15 K/cm. Then, the ingot can be cooled at a rate of up to ~30-50 K/hour until 723 – 643 K is reached. In this range, the crystallization of any Te inclusions takes place; therefore, the next phase should be conducted at a slower rate.

3. CONCLUSIONS

The melting and crystallization of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ occur non-isothermally but in certain discrete temperature intervals. The range of the last are defined both by the melt's composition and its «thermal prehistory». The important factor controlling the nucleation process is the kinetic features of the local thermodynamics equilibrium established between layers with different ordering. The degree of supercooling in the stoichiometric $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ melt increases gradually with overheating, and remains constant at temperatures higher than 20 K. We also demonstrated that the melt structure formed at high temperatures is maintained during the subsequent reduction of the melt temperature, while its intermediate structure is destroyed according to the extent of overheating.

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