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Growth and characterization of $Cd_{1-x}Zn_xTe$ crystals with high Zn concentrations

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Abstract

The crystalline quality of large grain size $Cd_{1-x}Zn_xTe$ with high Zn concentrations ($0.45 < x < 0.85$) grown by a zone melting process was investigated using photoluminescence, X-ray diffraction, optical transmission and micro-Raman measurements. We have found that extrinsic and intrinsic factors lead to Zn segregation encountered in both the radial and the longitudinal directions. The degree of segregation depends on the nominal Zn concentration. In addition, small precipitates of tellurium are found in the regions with low Zn concentrations in the solid solution. Such precipitates are absent in regions with high Zn concentrations. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The II–VI compounds have given rise to several investigations in the last few decades due to their multiple applications in technological devices. Special interest has developed the $Cd_{1-x}Zn_xTe$ system; known to be a good candidate for lattice matched substrates for growth of HgCdTe and HgZnTe epitaxial thin films [1]. In addition, $Cd_{1-x}Zn_xTe$ and CdTe crystals are important materials for the development of high-resolution far infrared and radiation detectors [2,3]. The quality of the epitaxial layer is strongly dependent on both the crystalline perfection and the chemical homogeneity of the substrate. Theoretical calculations suggested that the addition of zinc to CdTe would stabilize the Cd–Te bond and that the $Cd_{1-x}Zn_xTe$ solid solution would therefore grow with a lower dislocation density [1]. These predictions have

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been supported by reports of improvements in the material structural quality with the addition of zinc [2]. Furthermore, for low Zn concentration ($x < 0.3$), an observation of a direct correlation between the crystalline quality and thermal parameters, such as thermal conductivity and diffusivity was made [4].

Numerous growth methods have been used to prepare large band gap II–VI ternary compounds. This is due in part to the different thermal characteristics of the separated components, but more importantly to the difficulties of obtaining truly single-crystal material of significant size, especially among those having a cubic structure [5]. In general, large diameter semiconductor single crystals are desired for applications. The growth of II–VI compound single crystals has several difficulties compared to the IV and III–V compounds [5,6]. The main difficulty is the lack of control of the melt–solid interface shape. The dissipation of the latent heat during the solidification is slow due to the relatively low thermal diffusivity and thermal conductivity as in the case of CdTe [4,7]. For $Cd_{1-x}Zn_xTe$ some additional difficulties in obtaining large size grains (crystals) are (1) the large lattice mismatch, of about 6.4%, between CdTe (6.4810 Å) and ZnTe (6.1037 Å) [8–10], that may cause strain in the developing lattices unless microscopic uniformity is achieved. (2) The low stacking fault energy, that promotes the generation of twins due to various factors, such as the high sensitivity to temperature fluctuations during crystal growth. (3) The large difference in the thermal conductivity and diffusivity between CdTe and ZnTe, for both the solid and liquid phases, that can be the origin of phase segregation [4,7], and (4) the segregation coefficient of zinc, being larger than unity ($k = 1.35$), that generally results in variations in zinc concentration along the crystal [11].

Most of the effort on this system has been concentrated on material for low x values. In part, this is motivated by the fact that the lattice-matched condition for the most commonly used HgCdTe films is met at low x values. Material with higher values would be useful for HgZnTe films grown for mid-infrared applications. It would be useful to investigate higher x values, since the band gap is higher; this leads to higher resistivity material, of importance for radiation detectors. Operation at higher temperature becomes more favorable, an important factor for geological applications, such as borehole logging, where temperatures $>300°C$ are often encountered. The growth of $Cd_{1-x}Zn_xTe$ alloys in single crystal form with high x values is difficult by any bulk technique, especially the rapid melt growth techniques, and especially at larger diameters. Material with $x > 0.4$ seems to be rare in bulk form; even at $x = 0.4$, quality is poorer than at lower x values. Vapor growth has been successful at low x values, but the low vapor pressure of tellurides makes it difficult to grow large crystal [12]. High-pressure Bridgman growth has yielded good material with 15 mm diameter at low x values, but even at $x = 0.4$ problems ensued [13].

2. Experimental procedure

2.1. Growth method

For binary or small x value ternary compounds, a Bridgman method might be preferable. However, at larger x values, normal freezing predicts that segregation will be difficult to overcome. A zone melting (zone leveling) method might be preferable, as has been demonstrated for sulfides and selenides [14]. This process was developed for these higher melting compounds (e.g. ZnSe melts at about 1520°C), and was adapted for CdZnTe with some changes in detail as described below. Another advantage of this method is that it has the potential for achievement of a convex interface during growth. The crucible-coil arrangement, with schematic temperature profiles, is shown in Ref. [14], for these experiments, a longer crucible was used.

High-purity polycrystalline compounds in chunk form (Cerac Inc., Milwaukee, Wisconsin) were used as the source materials. In operation, the charge contained in the graphite crucible is lowered through the induction coil. The average boule diameter was about 2.5 cm determined by the taper of the crucible. The maximum temperature at the outside of the crucible was estimated to be about 1350°C. The gradient below the coil is approximately 70°C/cm; the interfaces convex towards the melt have always been in the case of selenides. An

external argon pressure of about 1000 KPa was applied. A two-step process is used: the first step is for consolidation, and the second one for recrystallization; the charge is molten in both steps [15]. An average rate of 12 mm/h was used in the second step, with a slightly slower rate used at the start. In general, the zone melting growth process is shown to provide ingots with good axial uniformity, but it is possible that, in tellurium-based systems, radial segregation is induced by a radial temperature gradient in the melt. The possibly higher level of association in tellurium-based melts could result in growth of more zinc-rich material at the outside of the boule, due to the possibility that there is more dissociation at the hotter outer region of the melt. It is possible that reduction of the convexity by increasing the maximum zone temperature would improve the situation.

2.2. Characterization

Crystallinity was determined by X-ray diffraction using a Siemens D5000 diffractometer operating at 35 kV, 15 mA with Cu K_α line. The peak width was measured at its center of gravity in the [1 1 1] direction and calculated using the Socavin II program. The zinc concentration was checked from the nominal value through the determination of the lattice constant by X-ray powder diffraction, by chipping small pieces along the radial direction of each wafer (nine positions), that was finely ground to have the powder consistency required. The composition was determined assuming the validity of a linear dependence between lattice constant and x fraction of Zn (Vegard's law). For a more precise determination of the lattice constant we used silicon as an internal standard. In all the samples measured, only the zinc-blende structure was detected. Crystals with starting composition ratios of Cd/Zn equal to 30/70 ($x = 0.7$) and 50/50 ($x = 0.5$) were used. Both lattice parameter and the full-width at half-maximum (FWHM) were determined for each one of the slices. To have a better determination of the zinc concentration, the X-ray analysis was done in both sides of the wafers. In order to determine the crystalline quality of the ingots, small samples from each surface of each slice were measured using X-ray diffractograms and, hence, the FWHM of the [1 1 1] diffraction lines was obtained.

In photoluminescence (PL) measurements we used an Ar^+ ion laser emitting in the blue (488 nm). The laser beam was focused onto the sample surface using a cylindrical lens. Since the relative intensity of different lines may depend on both the intensity of the excitation source and the sample temperature, the photon flux and the sample temperature were kept constant at approximately 1×10^{17} photons $cm^{-2}\,s^{-1}$ and 12 K, respectively. The PL measurements were carried out using an Air-Products closed-circuit helium refrigerator, and the emitted radiation was spectrally analyzed using a Jobin Yvon double monochromator model HRD-100 set with a resolution better than 0.05 nm.

3. Results and discussion

In this work we have studied polycrystalline $Cd_{1-x}Zn_xTe$ ingots of about 2.5 cm diameter and 9 cm length. The average grain size was several millimeters. In particular, two ingots were carefully analyzed, the nominal charge composition were Cd (0.25), Zn (0.25) and Te (0.50) for ingot 1, and Cd (15), Zn (35) and Te (50) (atom %) for ingot 2, respectively. However, the measured Zn concentration along both the length and the radial directions was not uniform in either of the ingots. Both ingots were sliced perpendicular to the length axis into wafers of 2.5 cm diameter and 2.0 mm thick. Four types of evaluations were performed on the different wafers at several positions along the radial direction: X-ray diffraction, optical transmission, photoluminescence and micro-Raman spectroscopy.

Fig. 1 shows the powder X-ray pattern in the range from 23 to 26° in the 2θ scale for a $Cd_{1-x}Zn_xTe$ sample, which corresponds to one of the 14 slices cut from ingot 1. The line corresponds to the [1 1 1] diffraction peak. The pattern at the upper left corner of Fig. 1, shows beside the [1 1 1]$Cd_{1-x}Zn_xTe$ diffraction line, the [1 1 1] diffraction line for silicon used for lattice calibration. Using that procedure a precision of about 0.1% for the determination in the lattice constant was possible. Doing this analysis for all the wafers from

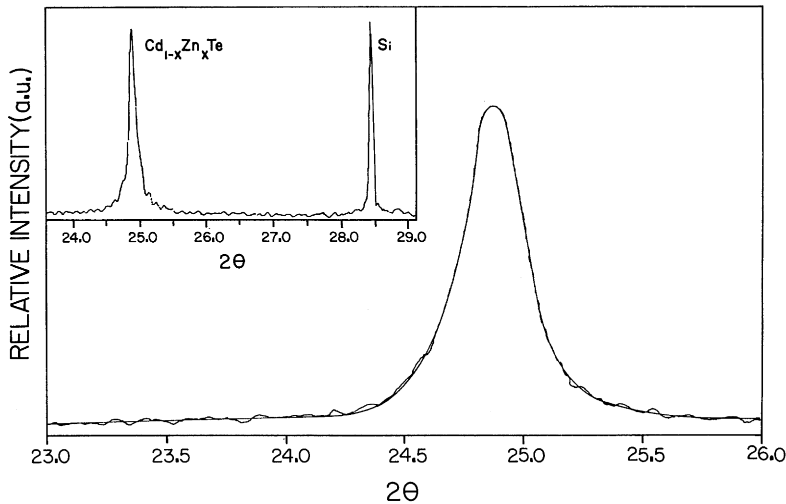

Fig. 1. Typical powder X-ray diffractogram of peak (1 1 1) in a $Cd_{1-x}Zn_xTe$ sliced sample. The broken line is the experimental result, the smooth line is the fit using Socavin II program. The inset illustrates the (1 1 1) peak of CdZnTe sample and the (1 1 1) peak belonging to single crystal Si used for lattice calibration.

ingot 1, we have determined two sections that are chemically different: one of these sections, from the upper part of the ingot, was found to have a zinc concentration lower than the nominal composition. The section was approximately 15% of the length of the ingot. The other section had zinc concentration between 24 and 27% of the total atomic concentration. The lower zinc concentration at the upper part of the ingot could be due to zinc segregation. In the rest of the ingot, the zinc compositional gradient is much lower, being exceptionally good at its central part, with a zinc compositional gradient of less than 0.8%/cm, which is smaller than in previous reports [8]. The radial composition was also examined and small radial gradients were found. For ingot 2 the structural analysis was also carried out for each one of the cut wafers, chemical gradients being found in both the longitudinal and radial directions. For high Zn concentration, the zinc distribution in the ingot 2 was analyzed by using optical transmission measurements.

Fig. 2 shows the X-ray pattern for a wafer belonging to ingot 1, in which tellurium precipitates with a [0 1 1]-preferred orientation were observed. Lines belonging to tellurium can be identified by the asterisk on top of them. Using micro-Raman we have also detected tellurium-rich regions in wafers from ingot 1 having intermediate Zn concentrations. Nevertheless, wafers from ingot 2 do not show the existence of tellurium precipitates. The segregation of tellurium in pure CdTe prepared by the same method was also observed by the micro-Raman measurements. In this case, the tellurium is clearly segregated forming precipitates with size between 1 and 10 μm. Similar results for CdTe have been reported [16,17]. From this analysis one can conclude that the incorporation of Zn reduces Te crystalline phase segregation in the $Cd_{1-x}Zn_xTe$ system. On the other hand, the Zn concentration along the length axis of the ingot 1 varied from approximately 20–30 at% and from 32 to 42 at% in ingot 2.

The results of the crystalline quality, proportional to the inverse of the FWHM, as function of composition is shown in Fig. 3. These results were obtained from the [1 1 1] diffraction line. As can be seen, despite the scattering of the data points, the crystalline quality gradually increases as the zinc concentration increases. In the same figure, values for both CdTe and ZnTe binary compounds are shown, that allows the comparison of the behavior of the measurements on our $Cd_{1-x}Zn_xTe$ materials. The results shown in this figure are in good

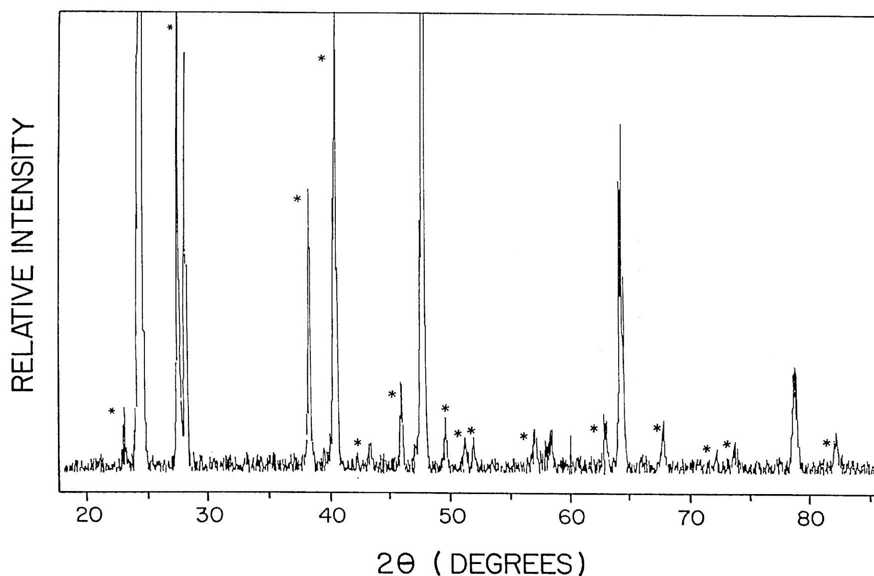

Fig. 2. X-ray diffraction pattern of $Cd_{1-x}Zn_xTe$ with Te precipitates. Asterisks denote peaks belonging to a segregated crystalline Te phase.

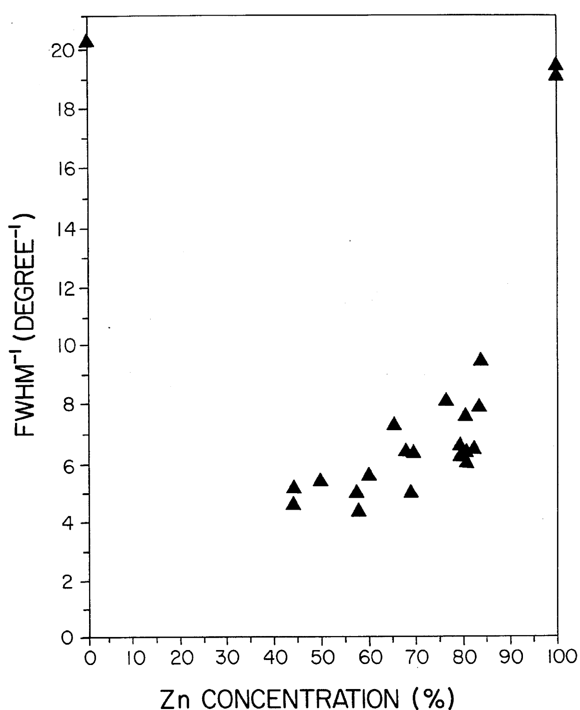

Fig. 3. $FWHM^{-1}$ of CdZnTe slices plotted as a function of the Zn content (x).

agreement with previous investigations on MBE epitaxially grown $Cd_{1-x}Zn_xTe$ films on GaAs substrate [18].

Light transmission through the sample was carried out using a white light collimated beam of about the same size as the 25-mm diameter wafer. The beam is perpendicular to the wafer. Figs. 4a and b show photographs of the transmitted light from two different wafers, both with a thickness of 2 mm. The darker central part of the wafer evidences no transmitted visible light and the outer part of the wafer shows transmission of red light indicating a larger band gap and therefore a larger Zn concentration. Also, the transparency reveals that Te precipitation cannot be significant, since Te precipitates, with their large scattering power and absorption, would render the material opaque. In order to determine more precisely the radial Zn concentration, photoluminescence measurements were taken at different positions along a line from the outer to the center of the wafer. Fig. 5 shows typical PL results in the excitonic region. Spectrum 0 corresponds to the outside part of the wafer and the numbers 1, 2, 3, 6, 8 and 9 in the spectra correspond to the number of millimeters from

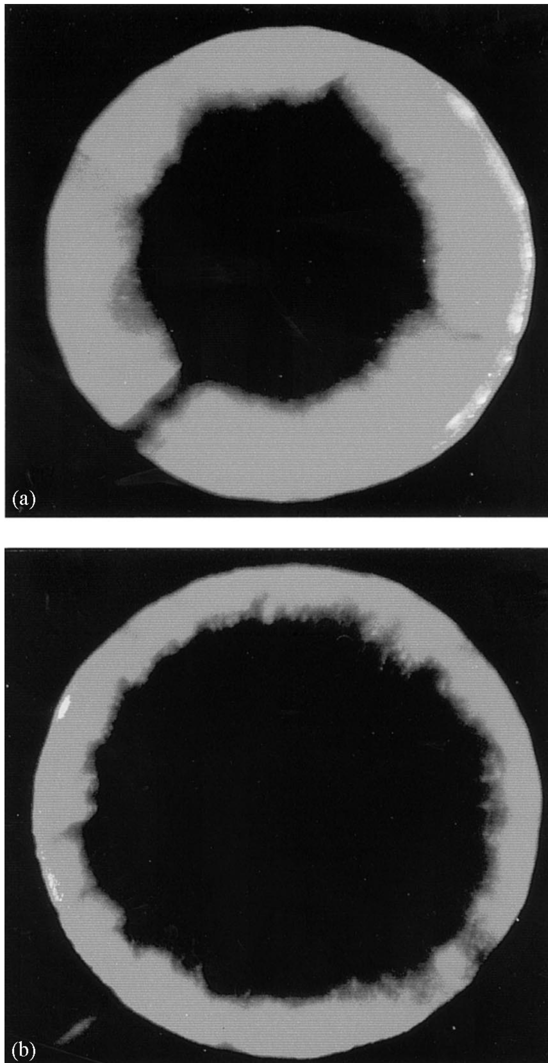

Fig. 4. White light transmission of two $Cd_{1-x}Zn_xTe$ studied slices. Here (a) and (b) indicate samples from the top and from the central part of the ingot, respectively.

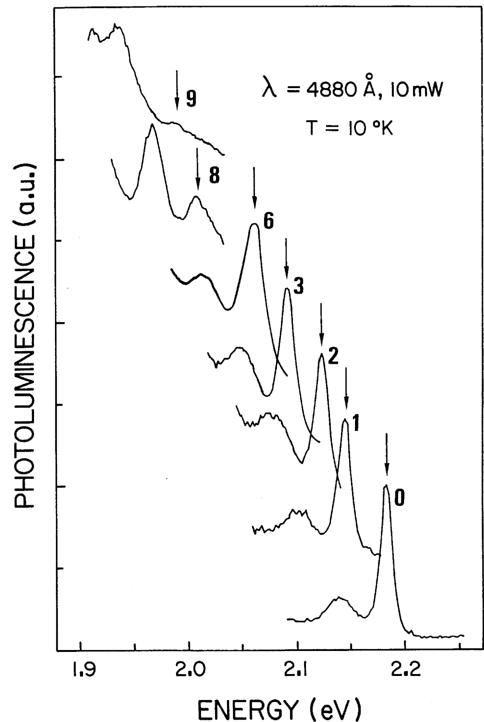

Fig. 5. Photoluminescence in a typical $Cd_{1-x}Zn_xTe$ wafer studied. The spectra show the excitonic peak transition measured along radial positions. Numbers on the top of each excitonic peak indicate the distance in mm from the border of the wafer towards its center.

the outside part of the sample towards the center where the measurements were taken. The curves have been shifted up for a clearer comparison. It can be observed that the intensity of the excitonic transition decreases as one looks at positions closer to the center part of the wafer, and that its FWHM value is increasing correspondingly. The latter agrees with the X-ray diffraction data in the sense that an increase in the Zn concentration results in an increase in crystalline quality. The zinc concentration (x) from the PL measurements was calculated using the expression $E_{BE} = 1.5932 + bx + cx^2$ [18,19], where E_{BE} is the measured energy of the bound exciton. The 1.5932 eV value was measured for high-quality CdTe and b and c are adjustable parameters (0.614 and 0.166, respectively). The exciton linewidth is in very good agreement with the linewidth measured for MBE material of the same x value [19]. Thus, it seems likely that the *microscopic* homogeneity is good, but that the *macroscopic* composition varies in both directions, although the axial composition is uniform for an appreciable portion of the boule. The shape of the phase diagram, similar in all Zn and Cd chalcogenides [20], has a peak at the stoichiometric composition that is not seen in the corresponding III–V compounds. This has been interpreted as evidence

of association in these melts [21]. Nevertheless, this technique has enabled us to make alloys such as CdZnSe and others with constant composition [22]. Both ZnTe and CdTe have melts that show semiconducting behavior well above the melting point (CdTe: 120°C, ZnTe: 60°C), and appear to have an appreciable "chain structure" in the melt [23]. Thus, it is possible that the outer part of the melt, being hotter, has less Cd concentration, since the Cd migrates into the center, where "chains" are more stable.

Using X-ray diffraction, optical transmission and PL measurements, a three-dimensional determination of Zn concentration and crystalline quality has been done for both ingots. For instance, ingot 2 shows two concentration zones with higher Zn concentrations in the outer zone. The Zn concentration gradient is less than 10%/cm for the outer zone and more than 20%/cm for the inner zone. The radial Zn segregation, in Zn rich ingots, is influenced by intrinsic and extrinsic factors as mentioned above. Probably the most important intrinsic factor is the large difference in the lattice constant, about 6.4% between ZnTe and CdTe. Another intrinsic factor is the difference between the thermal conductivity and diffusivity [3,18], and even more importantly, its larger decrease in a concentrated alloy. The associate nature of tellurides, and their consequent similarity in both the liquid and solid phase [23], make it likely that the thermal conductivity of these concentrated alloys in both the liquid and solid phases is very low. Thus, it is possible that small temperature gradients can easily form, and lead to concentration gradients in the solid. This is couple to an extrinsic factor, to use of a zone melting technique, with its relatively large gradients. Although this has given uniform material in the case of the higher-melting sulfides and selenides [14], it is possible that, in unmodified form, it is not optimum for the growth of concentrated telluride alloys, especially of this diameter. A lower rate of growth, however, might help, as well as the use of a larger charge, leading to a longer ingot; this has resulted in improved boule quality in the case of other materials. The shallow gradient Bridgman approach, so beneficial for III–V compounds, inherently gives a concentration gradient in the case where the segregation coefficient differs appreciably from unity. Thus, it would seem that zone melting has an intrinsic merit. In fact, the traveling heating method (THM) [8] could be called "off-stoichiometric zone melting"; a large excess of Te is used. This method would inevitably have appreciably lower growth rates, and it could have difficulty with Te precipitation, because of the Te excess. Nevertheless, THM or a hybrid of it with our "stoichiometric" zone melting, perhaps with another "solvent", would be worthy of consideration. The lower growth temperature might retard precipitation, and, as has been stated above, the higher zinc concentration apparently leads to the elimination of Te precipitation. Thus, a more concentrated THM, "near stoichiometric zone melting", with the assistance of a solvent component such as a salt or metal, might solve the microscopic homogeneity problem while preserving a precipitate-free condition. An extrinsic factor, in these particular materials, using the method used to grow them, is a dynamic problem during the cooling, originated by heat diffusion in both directions, radial and longitudinal, causing the Zn segregation as observed. It appears that *microscopic* homogeneity has been achieved at this high x values, but that *macroscopic* homogeneity remains to be achieved. This seems to be true for melt grown tellurides in general; in contrast, epitaxial films of many semiconductor compounds can often be grown with both types of homogeneity. This may be due to the low thickness of epitaxial films, or their low growth temperature and growth rate. Lower rates in melt growth might help.

In the telluride case, in contrast to the selenide or sulfide case, a concentration gradient appears to be readily obtainable in a wide melt. This is surprising in view of the low viscosity [23]; possibly, Cd-rich, more highly associated material exists in the center of the melt. This may also account for the poorer structure at the center, as evidenced by the width of the exciton lines. A "coring" effect is common in melt grown crystals of many types.

4. Conclusions

In summary, $Cd_{1-x}Zn_xTe$ large grain polycrystalline materials grown by a zone melting process

have been characterized using X-ray diffraction, photoluminescence and transmission measurements. Utilizing these measurements, a three-dimensional mapping of Zn concentration has been achieved. It is found that Zn segregates in both the radial and longitudinal directions and that the degree of segregation depends on the nominal Zn concentration. It was also found that the tellurium precipitates to a degree that depends on the Zn concentration, i.e., large Te aggregates are observed in pure CdTe and the precipitates are reduced with the increase of Zn concentration. In samples with high Zn concentration no precipitates were observed.

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