## Growth of Solid Solution Single Crystals

Dr. Sandor L. Lehoczky, Principal Investigator
NASA Marshall Space Flight Center
Mail Code ES75
Marshall Space Flight Center, AL 35812
Phone: (256) 544-7758
Fax: (256) 544-8762
E-mail: sandor.lehoczky@msfc.nasa.gov

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Co-Investigators:
Dr. Frank R. Szofran, NASA Marshall Space Flight Center
Dr. Donald C. Gillies, NASA Marshall Space Flight Center
Mr. Dale A. Watring, NASA Marshall Space Flight Center

The objective of the study is to establish the effects of processing semiconducting, solid solution, single crystals in a microgravity environment on the metallurgical, compositional, electrical, and optical characteristics of the crystals. The alloy system being investigated is the solid solution semiconductor $Hg_{1-x}Cd_xTe$, with x-values appropriate for infrared detector applications in the 8 to 14 mm wavelength region. Both melt and Te-solvent growth are being performed. The study consists of an extensive ground-based experimental and theoretical research effort followed by flight experimentation where appropriate. The ground-based portion of the investigation also includes the evaluation of the relative effectiveness of stabilizing techniques, such as applied magnetic fields, for suppressing convective flow during the melt growth of the crystals.

The difficulty of growing bulk crystals of the alloys, with both radial and axial homogeneity of significant lengths in Earth's gravity is well documented. Because the HgTe-rich component rejected during solidification is more dense, the vertical Bridgman-Stockbarger growth process would appear to be both gravitationally and thermally stable against convection, but this is not generally true. Due to the peculiar relationships between the thermal conductivities of the melt, solid, and ampoule, it is practically impossible to completely avoid radial temperature gradients in the growth region. In general, the presence of radial temperature gradients near the growth region will cause a curvature in the solid-liquid interface which need be neither an isothermal nor an isoconcentrational surface. Furthermore, the growth of high quality crystals usually requires a slightly convex growth interface as viewed from the melt. Under the influence of stable growth conditions, such interface geometries readily lead to lateral alloy segregation because of the tendency of the more dense HgTe-rich liquid to settle at the portions of the surface having the lowest gravitational potential. Because the alloy solidus temperature decreases with increased HgTe content, the interface temperature will be lowered in this region, causing the interface curvature to increase. Although lateral diffusion will tend to drive the interfacial melt compositions to some equilibrium values, most ground-based melt-growth experiments show large radial compositional variations that are probably a direct consequence of such an interfacial fluid flow phenomenon. In low gravity it is expected that the highly desired slightly convex growth surfaces will be easier to maintain because of the reduced tendency for stratification of the denser (HgTe rich) fluid component. At the same time, the near-elimination of radial temperature gradient-driven convection is expected to provide for a better control of the lateral compositional distribution in the melts.

It is thus expected that by growing under the influence of low-gravity conditions ($g < 10^{-6} g_0$), crystals with significantly improved crystallinity and compositional homogeneity can be prepared as compared to the best crystals that can be produced on Earth. It is also reasonable to expect that careful characterization of both the space- and ground-grown materials will lead to better insights into the peculiarities of the various growth mechanisms that will permit improvements in Earth-based processing of $Hg_{1-x}Cd_xTe$ and other compound semiconductor alloy systems.

It is believed that CdTe, $Hg_{1-x}Cd_xTe$, etc. probably possess extremely small yield strengths near their growth temperatures. If this is the case, the high dislocation density ( $\sim 10^5$ $cm^{-2}$) usually seen in these crystals could be due at least in part, to stresses induced by the samples own weight, that is, self-induced stresses. Therefore, a second goal of these experiments is to assess the validity of this hypothesis.

Over the past several years, a detailed evaluation has been performed on the effects of growth parameters on the axial and radial compositional uniformity, defect density, and optical properties in directionally solidified $Hg_{1-x}Cd_xTe$ and other similar compounds and pseudo-binary alloys. A series of $Hg_{1-x}Cd_xTe$ alloy ingots ($0<x\leq0.6$) has been grown from pseudobinary melts by a vertical Bridgman-Stockbarger method using a wide range of growth rates and thermal conditions. Several of the experiments were performed in transverse and axial magnetic fields of up to 5T. Precision measurements were performed on the ingots to establish compositional distributions and defect density distributions for the ingots. Correlation between growth rates and thermal conditions and growth interface shapes have been established for the alloy system. To assist the interpretation of the results and the selection of optimum in-flight growth parameters, the pseudobinary phase diagram ($0\leq x\leq1$), liquid and thermal diffusivities ($0\leq x\leq0.3$), melt viscosity, and the specific volumes as a function of temperature ($0\leq x\leq0.2$) have been measured. From these measurements and other available data, the heat capacity, enthalpy of mixing, and the thermal conductivity of pseudobinary melts have been calculated using a regular associated solution model for the liquid phase. A one-dimensional diffusion model that treats the variation of the interface temperature, interface segregation coefficient, and growth velocity has been used to establish effective diffusion constants for the alloy system. Theoretical models have been developed for the temperature distribution and the axial and radial compositional redistribution during directional solidification of the alloys. These were used along with the experimental results to select the parameters for the first flight experiment flown on the Second United States Microgravity Payload (USMP-2) mission. A microscopic model for the calculation of point-defect energies, charge-carrier concentrations, Fermi energy, and conduction-electron mobility as functions of $x$, temperature, and both ionized and neutral defect densities has been developed. For selected samples, measurements were performed of electron concentration and mobility from 10-300 °K. The experimental data were in reasonably good agreement with theory and were successfully analyzed to obtain donor and acceptor concentrations for various processing conditions.

A five zone Bridgman-Stockbarger type "Advanced Automatic Direction Solidification Furnace (AADSF)" has been designed and developed for the flight portion of the investigation. The AADSF was successfully flown on the USMP-2 mission in March 1994 during which a 15 cm long and 0.8 cm diameter $Hg_{0.8}Cd_{0.2}Te$ alloy crystal was grown under precisely controlled residual acceleration conditions over a period of approximately 11 days. Detailed microstructural and compositional analysis has been performed for the crystal. A rate change inserted into the growth timeline sequence produced in the crystal an effective time marker for correlating orbital and residual accelerations to various crystal features and alloy compositional changes. This allowed a detailed evaluation of the effects of the magnitude and direction of residual acceleration on crystal homogeneity and perfection to be made for the <u>first time</u>. Circumferential variation of composition and topographic features around the boule indicated that residual acceleration vectors were present and have a large effect on the growth process. The magnitude of the measured transverse compositional variations along the growth axis showed a high degree of correlation to the direction of the residual acceleration vectors. X-ray topographs of the portion grown in the most favorable attitude (-XLV, -ZVV) indicate that this region is of significantly higher quality than usually grown on the ground. The Orbital Acceleration Research Experiment (OARE) acceleration measurement instrument record of residual acceleration vectors proved to be in excellent agreement with our results, as evidenced by the surface features of the boule. Certain attitude maneuvers of the orbiter can dramatically affect the growth stability. This is illustrated by the roll-around in tail-down attitude which reversed the direction of the residual acceleration perpendicular to the interface and caused thick compositional striations at 11 cm along the crystal. Further microstructural, optical, and electrical characterizations of the crystal promise to provide a wealth of additional information on the growth in low earth orbit of solid solution alloy crystals having a large separation between their liquidus and solidus. A series of $Hg_{0.8}Cd_{0.2}Te$ crystals were also grown under the influence of axial magnetic fields up to 5T. The application of the magnetic fields greatly reduced the radial compositional variations in the crystals, further underlying the importance of gravitationally-induced fluid flows. A new seeded method has been developed and was used for the Bridgman growth of an x=0.16 alloy input during the USMP-4 STS-mission. An <111>-B oriented CdTe seed was used along with a specially prepared alloy charge that emulated the calculated steady-state melt composition profile upon back melting. The results analysis of the results from the experiment are in progress.