Semiannual Technical Progress Report for:
**"Mercuric Iodide Research and Development
in Support of DOE Historically Black
Colleges and University Program"**

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EXECUTIVE SUMMARY

This report describes the progress achieved during the first six months of the program. The different subjects studied were:

- a) Zone refining experiments of mercuric iodide to establish optimum refining parameters and produce purified material.
- b) Development of surface reflection spectroscopy as a method to measure crystal surface temperatures, with emphasis on investigating the potential of using optical multichannel analysis.
- c) Optical Methods for Measuring Iodine Vapor During Physical Vapor Transport of HgI_2
- d) Atomic Force Microscopy Studies

"Mercuric Iodide Research and Development in Support of DOE Historically Black Colleges and University Program"

A) Zone refining experiments of mercuric iodide to establish optimum refining parameters and produce purified material.

The zone refining technique is one of the steps used during the purification of the mercuric iodide starting material. It is presently being performed in a laboratory built apparatus that includes a narrow (2.5 cm) high temperature heater. The lead iodide material is loaded in silica ampules, evacuated and sealed. After ≈ 100 passes at 1.5 cm/h, the process will be stopped and the HgI_2 ingot will be removed. The central part of the ingot is the purest part of the ingot (impurities having a distribution coefficient differing from unity will accumulate at the extremities of the ingot).

Modifications have been made in the experimental setup to allow for vertical refining. Efficient mixing of the fluid, as it occurs under the conditions of gravity induced convection, is crucial to zone refining process. In the vertical configuration the convection is dramatically increased and will result in an improved separation of impurities. Several technical difficulties had to be overcome (better thermal insulation of the ambient oven, improved heater configuration to avoid smearing (broadening) of the thermal profile. The setup was successfully tested and two experiments were completed.

B) Development of surface reflection spectroscopy as a method to measure crystal surface temperatures, with emphasis on investigating the potential of using optical multichannel analysis.

Previous evaluation of the SPEX Triplemate spectrophotometer equipped with a multichannel CCD detector revealed that although much faster accumulation times are required to obtain reflectivity spectra, the signal to noise ratio was still limited by the saturation of the CCD detector at levels of 6×10^5 counts per channel.

The operation of the instrument in a new upgraded mode that provides data averaging has shown that by averaging 20 spectra, (each with an integration time of 1 sec) an improvement by almost a factor of two in the error of the determination of the peak position of the reflectivity peak (and therefore in the determination of the surface temperature) was achieved.

C)Optical Methods for Measuring Iodine Vapor During Physical Vapor Transport of HgI₂

Optical methods have been established for in-ampoule measurements of the iodine vapor concentration during the growth of mercuric iodide (HgI₂) single crystals by physical vapor transport (PVT). Significant concentrations of iodine vapor, which can vary during the growth period, occur in some ampoules. The absorptivity of iodine vapor at 514 nm is $7.7 \cdot 10^5 \text{ cm}^2 \text{ mol}^{-1}$. Differential Scanning Calorimetry (DSC) measurements correlate with vapor absorption and indicate the presence of free crystalline iodine in vapor-grown HgI₂.

Consider a transparent ampoule containing an absorbing medium. The transmitted intensity I is related to the absorbance A by $A = \ln (I_0/I)$, where I_0 is the intensity transmitted when there is no absorption. The absorbance and the vapor density are related in the conventional way by Beer's Law,

$$A = \alpha' d \rho \quad (1)$$

where α' is the absorptivity which depends only on the type of vapor, d is the path length, and ρ is the vapor density. In circumstances where Beer's Law is not obeyed, α' can be taken as having some apparent dependence on vapor density, $\alpha'(\rho)$.

Using the well justified assumption that iodine is an ideal gas at the concentrations of interest,⁽¹⁰⁾ the partial pressure P and Kelvin temperature T are related by $P = \rho RT/M$, where R is

the gas constant and M is the molar mass of I_2 . The partial pressure of I_2 over solid iodine has been determined experimentally ⁽¹¹⁾ and is given by

$$\log_{10}[P(\text{torr})] = 9.9543 - 3103.7/T \quad (2)$$

The absorbance, $A = \ln(I_0/I)$, can be measured for a set of calibration ampoules of known dimension d and iodine vapor densities ρ . A plot of A versus ρ yields a master curve $A(\rho)$ from which unknown vapor densities in experimental ampoules can be obtained from measurements of their I_0/I values. If Beer's Law is obeyed as in equation (1), the curve is linear and passes through the origin, and the absorptivity α' may be found from the slope.

The constant transmission above the saturation temperature, where the density is constant, shows that the absorption spectrum depends explicitly on density and not on temperature, which affirms a basic assumption of the absorption method. The saturation temperature T_s is related to the iodine mass m through the ideal gas law and equation (2) by

$$m = \frac{MV}{RT_s} \cdot 10^{9.9543 - \frac{3103.7}{T_s}} \quad (3)$$

where V is the ampoule volume and R is in appropriate units. The known behavior of iodine as an ideal gas, along with the wide applicability of Beer's law, generally would predict a linear dependence. The line of best fit at low densities has been obtained and is given by equation (4),

$$A = 7.3 \times 10^{-3} \rho \quad (4)$$

where ρ has units of $\mu\text{mol l}^{-1}$.

The absorptivity α' of iodine vapor may be calculated from equations (1) and (4), using the representative value of 9.6 cm for the ampoule diameter, and is given by $\alpha' = 7.7 \cdot 10^5 \text{ cm}^2 \text{ mol}^{-1}$.

D) Atomic Force Microscopy Studies

Atomic force microscopy (AFM) are underway to characterize the surface of semiinsulating

mercuric iodide and lead iodide crystals. The high vapor pressures of these compounds prohibit the use of techniques that require high vacuum conditions. Intrinsic defects and defects induced by surface preparation were imaged with high resolution. Both mercuric iodide and lead iodide are very soft materials and under certain conditions, mechanical deformations or material removal during AFM scanning in the contact mode were found to occur. Their avoidance, by using the microscope in the tapping mode of scanning, was investigated and the spatial resolution in the nanoscale range was also evaluated for both modes.

D) Impurity Distribution of Zone-Refined Mercuric Iodide by ICP-AES

Mercuric iodide single crystal is being developed for x-ray and gamma ray detectors applications where high-purity starting materials is required. Zone refining processing has been proven to be an effective step in the purification of large amounts of mercuric iodide for crystal growth. In this study we used the Inductively Coupled Plasma-Atomic Emission Spectroscopy, ICP-AES (performed at Sandia National Laboratories, with one of the Fisk students Leroy Salary participating in the measurements) to identify and determine the distribution of impurity concentrations along the ampule after zone-refining mercuric iodide. The results show that for Ag, Cu, Fe, Mg, Ca, Zn and Al, the zone-refining process does sweep the impurities to the last-to-freeze zone, due to an effective distribution coefficient, $k < 1$. For Na, Ni and Pb the concentration gradient seems to be fairly independent of the position along the ingot.