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A Review of Recent Measurements of Optical and Thermal Properties of α -Mercuric Iodide *

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The band gap energy of α -mercuric iodide was measured recently at elevated temperatures using optical absorption and reflection methods. In addition, reflection spectral measurements indicate that the temperature dependence of the exciton peak can provide a means of measuring, in a non-disturbing and remote manner, the local surface temperature of an α -mercuric iodide crystal during its growth from the vapor. Recent measurements of the thermal diffusivity and thermal expansion tensors have confirmed the anisotropy of this material and have implications for growth morphology and the generation of lattice defects.

1. INTRODUCTION

The knowledge of the physical properties of a crystal and their relation to the nature and content of defects are essential for both applications and fundamental reasons. Alpha-mercuric iodide (α -HgI₂) is a material which has found important applications as room temperature X-ray and gamma ray detectors¹. Some recent thermal and optical measurements of this material, using the samples of improved crystallinity which are now available, are reviewed below. Heretofore, these properties have received less attention than the mechanical and electrical properties, particularly at elevated temperatures. In the technology of α -HgI₂, where there is a continuing motivation to obtain larger single crystals without compromising the material quality, a better knowledge of the thermal and optical properties may lead to improvements in the processes of material purification, crystal growth and device fabrication.

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This paper reviews recent (1989-91) thermal and optical measurements of α -HgI₂ crystals conducted mainly at Fisk University and EG&G/Energy Measurements, Santa Barbara Operations. The results are listed in Table 1. The (recent) results refer to ambient temperature, but in every case measurements were also made at temperatures as close to the upper limit of phase stability of α -HgI₂, 127 °C, as was practical. Results of other (previous) studies at ambient temperature are also listed. The experimental methods and some implications for these recent measurements of the direct band gap energy and its temperature coefficient, the thermal diffusivity tensor and the thermal expansion tensor of this anisotropic material are reviewed and discussed. Recent work which demonstrates the use of reflectivity spectra for remote and practically non-invasive temperature measurement is also reviewed.

2. ENERGY BAND GAP

The first bandgap study of HgI₂² reported $E_g = 2.11$ eV at room temperature from diffuse reflection measurements on powdered and polycrystalline samples. Other values of 2.3707 eV (4.2K) by emission³, 2.369 eV (4.2K) by absorption⁴, 2.397 eV (2K) from wavelength modulated reflection⁵, and 2.27 eV (0K) for the direct gap and 2.203 eV (0K) for the indirect gap, both from photoconductivity⁶, have been obtained for low temperatures. The temperature coefficient of the bandgap has also been found, with values of $-14 \cdot 10^{-4}$ eV/K² and $-6.5 \cdot 10^{-4}$ eV/K⁷ in the elevated temperature range, 330 K to 400 K, and $-2.6 \cdot 10^{-4}$ eV/K⁸ and $-1.13 \cdot 10^{-4}$ eV/K⁹ in some lower temperature ranges. There are significant differences among these bandgap energy values and temperature coefficients, which may stem from different interpretations of the various data and from differences in

the purity and crystalline perfection of the material.

In a recent study ¹⁰, a single crystal of α - HgI_2 was grown to an approximate size of $20 \times 15 \times 10 \text{ mm}^3$ by physical vapor transport (PVT) using the EG&G/EM method ¹¹. The ampule was heated uniformly to various temperatures from 285 to 361 K, and a shiny, (001) crystal face was used to reflect collimated, white light to a monochromator and detection system. The band gap energy of single crystals of α -mercuric iodide was obtained for temperatures over the range from ambient to the limit of phase stability, 400 K. The method is based on measuring the spectral shifts of the excitonic reflection peak with temperature. Using the first reported measurement of the excitonic absorption peak at ambient temperature in this material ¹⁰, coupled with results for low temperatures from previous investigations, it was found that the direct band gap at 300 K is 2.292 eV. Values at higher temperatures were also obtained. The Varshni ¹² relation for the temperature dependence of the energy gap in semiconductors can be represented by:

$$E_g(T) = E_g(0) - \frac{\alpha'T^2}{T + \beta'} \quad (1)$$

where α' and β' are constants which are characteristic of the particular material, T is temperature in K and $E_g(0)$ is the energy gap at 0 K. When the $E_g(T)$ data was used with Eq. 1 to fit α' , β' and $E_g(0)$ as adjustable constants, it was found that:

$$E_g(T) = 2.370 - \frac{3.8 \times 10^{-4} T^2}{(T + 135)} \quad (2)$$

where $E_g(0)$ and $E_g(T)$ are in eV. Thus, the band gap energy at 0 K is given by $E_g(0) =$

2.370 eV. The temperature dependence of the energy band gap is linear from 400 K down to about 200 K, with a coefficient of $-3.9 \cdot 10^{-4}$ eV/K. The linearity in this temperature range agrees generally with other reported data ²⁷.

This recent band gap energy result, $E_g = 2.292$ eV, for the direct gap at 300 K, differs from Bube's ² value of 2.11 eV, obtained from the onset of exponentially increasing absorption, and from Lopez-Cruz's ⁶ values of 2.11 eV for the direct gap and 2.03 eV for the indirect gap, obtained by calculating ¹³ the absorption coefficient from photoconduction measurements at 300 K. However, the recent absorption spectrum does show that absorption at ambient temperatures does indeed begin below 2.1 eV, where Kanzaki et al ¹⁴ have also measured an exponential absorption tail. The result that $E_g = 2.292$ eV for the direct gap does not rule out the possibility of an indirect gap as well, with absorption effects at energies below 2.1 eV, as was discussed ¹⁰. Low temperature absorption spectra in the absorption tail region may be necessary for the complete elucidation of this issue. Nevertheless, the present results may find an immediate use in the interpretation of the structure of photoconductivity spectra and of the temperature dependence of the efficiency of α -HgI₂ photocells.

3. REFLECTANCE SPECTROSCOPY THERMOMETRY (RST)

The reflection spectrum measurements in the E_g study ¹⁰ indicated that the temperature dependence of the exciton peak could provide a means of measuring the surface temperature of a growing mercuric iodide crystal without disturbing the growth or interfering with the temperature, as might occur using a conventional temperature sensor. This technique can be called Reflectance Spectroscopy Thermometry (RST), and it is

surface specific, being based on reflectance, and is non-disturbing if a light beam of low power is used. The use of RST to measure surface temperatures of α -mercuric iodide crystals growing by PVT has been demonstrated recently¹⁵. The method has an accuracy of ± 1.5 °C in the present state of development and is applicable in quasi static situations. It is anticipated that higher accuracy and applicability to transient conditions can be achieved with further development. RST is particularly applicable to semiconductors at low enough temperatures where the exciton spectral structure is discernable, so it is a complementary technique to optical pyrometry.

4. THERMAL DIFFUSIVITY

Measurements of the thermal diffusivity¹⁶ tensor were made recently in α -mercuric iodide, a highly anisotropic material. The results were obtained in the temperature range of 20 - 80 °C, and they may be important for understanding and controlling the morphology and crystalline quality of crystals grown by physical vapor transport. The previous thermal conductivity data for this material were obtained at temperatures well below ambient¹⁷ or under conditions that did not resolve the expected anisotropy¹⁸.

In our recent study the thermal diffusivity was measured along the principal axes of single crystals of α -mercuric iodide grown by the PVT method. The experiments were based on the flash pulse method^{19,20,21,22,23}. Mercuric iodide wafers with a face area of 100 mm² and a thickness of 0.5-2.5 mm along either the [001] or the [100] crystallographic axes were prepared. A thin palladium (Pd) film was evaporated onto the back face, where a thermocouple was attached. A heat pulse was produced with a shuttered argon ion laser which was absorbed at the front face, and the temperature-time response (thermogram) at

the back face was recorded. The analysis is based on the expression¹⁹ for the thermal diffusivity, θ_0 , in the ideal case where heat losses are absent and the pulse is very short, as given by:

$$\theta_0 = 0.388d^2/t_{1/2} \quad (3)$$

where d is the sample thickness, and $t_{1/2}$ is the time for half the maximum temperature rise at the back face.

The thermogram was analyzed by the the method of Heckman²³, so as to include the actual heat loss and pulse width effects. The average results for different samples showed that the thermal diffusivity, θ , of α -HgI₂ is about 3.6 times larger along the a -axis than along the c -axis, as listed in Table 1. The thermal diffusivity, θ , and thermal conductivity, k , are fundamentally related by $k = \theta\rho c$. Using $\rho = 6.37 \text{ g/cm}^3$ ²⁴, and $c = 0.173 \text{ J/gK}$ ²⁵, the non-zero elements of the thermal conductivity matrix, $k_{11} = k_{22} = k_{[100]}$ and $k_{33} = k_{[001]}$, were calculated and are listed in Table 1, as $k_{11} = 4.08 \cdot 10^{-3} \text{ J/cmsK}$ and $k_{33} = 1.13 \cdot 10^{-3} \text{ J/cmsK}$, at 300 K. The measurements at 80 °C indicated that the thermal conductivities (or diffusivities) at vapor growth temperatures, 100 - 120 °C, are about one half as large as at ambient temperatures.

These recent thermal diffusivity results can be compared with the directionally averaged value of $\theta \approx 4.5 \cdot 10^{-3} \text{ cm}^2/\text{s}$ as obtained by Lanyi, et al¹⁸. The low temperature values of DeGöer et al¹⁷ can be informally extrapolated to give $\alpha_{[001]} \approx 2 \cdot 10^{-3} \text{ cm}^2/\text{s}$ and $\alpha_{[100]} \approx 5 \cdot 10^{-3} \text{ cm}^2/\text{s}$, which are larger than the recently obtained values.

The growth morphology of single crystals can be related to the anisotropy of the thermal diffusivity. As noted above and in Table 1, the results (recent) show that thermal diffusivity along the [100] or [010] lattice directions, θ_{11} , is about 3.6 times larger than along

the [001] axis, θ_{33} . Single crystals of α - HgI_2 grown by PVT in a cylindrical furnace by the EG&G/EM method¹⁰ typically are 3-6 cm on a side and are bounded mainly by {001} and {110} faces. The {001} faces are usually approximately vertical and are separated by the narrowest dimension of the crystal. The base is approximately elliptic, with the shorter axis being aligned approximately along [001] and being about 0.5 - 0.6 times as large as the longer axis. This shape can be partially understood from thermal diffusivity considerations. During growth there is a generally radial flow of heat from the furnace into the crystal faces and out through the center of the basal plane into the cold sink under the growth pedestal. The heat flow rate in any radial direction is proportional to $k\Delta T/d$ where k is the thermal conductivity (proportional to θ) and ΔT and d are the temperature difference and distance, respectively, between surface and the center of the base plane. Since ΔT must be nearly equal for all faces on a crystal which growing slowly at near equilibrium, and since the heat flows in all radial directions should be very similar due to symmetry, k/d should be invariant. Thus, the crystal width to length ratio would be expected to equal $\theta_{\{001\}}/\theta_{\{110\}} \approx 0.28$. In practice this ratio is 0.5 - 0.6, so there are apparently other factors influencing the morphology. Nevertheless, it seems clear that anisotropy of the thermal diffusivity is an important factor in determining the characteristic shape under these growth conditions. The shapes of crystals grown in an alternative orientation, with the {001} plane horizontal (top of crystal) rather than vertical, confirm this conclusion.

The thermal diffusivity also provides a measure of the thermal response time of a system to heat inputs, which is useful in processing. From general diffusion theory, the time constant τ is an approximate measure of the time required for a heat input pulse to be substantially transmitted a distance d away from the input, and is given by $\tau = d^2/\theta$.

Accordingly, abrupt changes in boundary temperature produced by temperature adjustments at the furnace wall or at the pedestal underlying the crystal will affect most of a 1 mm crystal in few seconds and most of a 1 cm crystal in few minutes, but will take more than an hour for a 2-6 cm dimensioned crystal. In terms of processing, τ^{-1} might be viewed as a maximum safe rate of cooldown from the growth temperature range, 100-120 °C, to avoid imposing significant transient temperature gradients.

THERMAL EXPANSION

α -HgI₂ has a tetragonal crystal structure, with a c-axis to a-axis ratio of 2.85, so a large degree of anisotropy in thermal expansion coefficient might be expected. However, until the recent work only the volumetric expansion had been measured, and values varied in the range, $60 - 140 \cdot 10^{-6} / ^\circ\text{C}$ ²⁶. Furthermore, these values were not obtained using the modern materials of better characterized purity. In the recent work²⁷, the expansion values along the principal crystallographic axes were obtained for single crystals as a function of temperature by precision X-ray diffraction methods with accurate temperature control. The measurements gave coefficients $\alpha_{33} = 54 \pm 5 \cdot 10^{-6} / ^\circ\text{C}$ along [001] and $\alpha_{11} = 11 \pm 4 \cdot 10^{-6} / ^\circ\text{C}$ normal to [001], as listed in Table 1.

Thermal expansion can be an important property because it is associated with the thermal stresses which are generally present during crystal growth. In methods of bulk growth a temperature gradient is necessarily present in the crystal and additional gradients are superposed transiently during cooldown. In general, temperature gradients give rise to thermal stresses whose magnitude depends²⁸ on αE , where E is the elastic modulus, and also depends on boundary restraints. During steady state growth, measurements made on

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ampules with affixed thermocouples have indicated that temperature differences of approximately 10 °C can typically occur between the crystal surface and the center of the base when the crystal is comparatively large. The parameter $\alpha E \Delta T$ is often used to estimate the order of magnitude of the thermal stresses in a system. The elastic modulus in any crystallographic direction can be calculated²⁹ from the six elastic constants³⁰ for this material. From these considerations $\alpha E \Delta T \approx 1.5$ MPa is an estimate of the stresses that are developed during steady state growth.

α -HgI₂ is a very soft material. The (001) planes shear easily, with an average yield stress³¹ of approximately 0.1 MPa, depending on direction. The three-dimensional thermal stress field will, in general, produce³² some resolved shear stress on planes in most orientations. Thus, it is likely that some (001) shearing and the attendant development^{33,34} of extended defects will occur during growth. These extended defects have been linked^{35,36} to reduced performance in devices made from this material. Further work is required in order to better predict the thermal stresses occurring in growing crystals.

One particular source of thermal stress is based on the interaction of the crystal with the pedestal during cooldown, and a simple calculation may be used to yield useful results. The source of stress is the difference in thermal expansion of the crystal and the glass pedestal, coupled with the crystal-to-pedestal adhesion which exists at the growth temperature. Assuming the interface is stress free at the time of growth, cooling over a range ΔT produces a stress, σ , which is given by $\sigma = (\alpha - \alpha_g) E \Delta T$, where $\alpha_g = 3.3 \cdot 10^{-6} / ^\circ\text{C}$ for glass and α , E and σ refer to a particular direction in the crystal plane adjacent to the glass. Since $\alpha_{33} > \alpha_{11} > \alpha_g$ the stress is characterized as an unbalanced biaxial tension in the plane, which means that shear components are present. As cooling proceeds, the tension

builds until either (i) stress relief occurs by plastic flow in the crystal, (ii) stress relief occurs by shearing at the interface, with the loss of glass/crystal adhesion, or (iii) the limit of cooling is reached. The maximum σ would occur if the stress relief did not occur before complete cooldown, $\Delta T = 100$ °C. From the elastic moduli referred to above, the maximum tensions can be calculated to be $\sigma \approx 50$ MPa along [001] and $\sigma \approx 10 - 20$ MPa in directions normal to [001]. Similar tensions occur if the crystal is oriented with other basal planes. In view of the much smaller yield stress for (001) slip, 0.1 MPa, it seems likely that enough resolved shear stress will result to produce significant plastic flow, regardless of the particular crystal orientation. On the other hand, there is some evidence that these stresses do not reach these maximum values because adhesion is broken before cooldown is complete. Work is underway to elucidate these matters.

From those considerations it appears that significant thermal stresses exist in a single crystal during steady state growth and during cooldown, no matter how slowly the cooling is done. Further work may provide guidance on how the growth process might be adjusted to minimize any adverse results from these stresses.

6. SUMMARY

Recent measurements of the band gap energy at room temperature and its temperature dependence, the thermal diffusivity, and the thermal conductivity of α -HgI₂ single crystals grown by physical vapor transport have been reviewed. The knowledge of these properties may lead to a better understanding of optical transitions, crystal morphology and crystal lattice defects. The measurement of the reflectivity spectrum as a function of temperature, which provides a non-disturbing method of obtaining surface temperatures with a precision of ± 1.5 °C, has been described.

TABLE 1. A summary of previous and recent values obtained for some optical and thermal properties of α -HgI₂ at ambient temperature.

Property	Experimental technique	Previous values and their reference	Recent values and their reference
Thermal conductivity, k , [Jcm ⁻¹ s ⁻¹ K ⁻¹]	-flash pulse	none	$k_{11} = 4.08 \cdot 10^{-3} \pm 3\%$, $k_{33} = 1.13 \cdot 10^{-3} \pm 10\%$ Ref. 15
Thermal diffusivity, θ , [cm ² s ⁻¹]	-steady-state -flash pulse	$4.5 \cdot 10^{-3}$, Ref. 18	$\theta_{(100)} = 3.70 \cdot 10^{-3}$, $\theta_{(001)} = 1.03 \cdot 10^{-3}$, Ref. 15
Bandgap E_g^{dir} , [eV]	-photoconductivity -reflectivity, -absorption	2.11, Ref. 2	2.292 ± 0.001 , Ref. 10
dE_g/dT , [eV/K]	-absorption -reflectivity	$-6.5 \cdot 10^{-4}$, Ref. 7	$-3.9 \cdot 10^{-4}$, Ref. 10
dE_g/dT , [eV/K]	-reflectivity	none	$-4.2 \cdot 10^{-4}$, Ref. 10
Thermal expansion α , (deg ⁻¹)	-X-ray diffraction	$2\alpha_{11} + \alpha_{33} = 60 \cdot 10^{-6}$, Ref. 26	$\alpha_{33} = 54 \pm 5 \cdot 10^{-6}$, $\alpha_{11} = 11 \pm 4 \cdot 10^{-6}$, Ref. 27

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