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CRYSTAL GROWTH AND ELECTRO-OPTICAL
CHARACTERIZATION OF BISMUTH TRI-IODIDE*

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CRYSTAL GROWTH AND ELECTRO-OPTICAL CHARACTERIZATION OF BISMUTH TRI-IODIDE

by M.M. Schieber, T.J. Davies, H.A. Lamonds,
W.F. Schnepple, P.T. Randtke, and R.C. Carlston

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ABSTRACT

The purification and crystal growth from the vapor phase and some electro-optical characterization measurements of BiI_3 are described. The sublimed boules had large single crystalline pieces which could be cleaved to give areas of about 1 cm in diameter and a thickness of about 1 mm. The grown crystals were measured for transmission from 0.6 μm to 50 μm , reflection from 0.6 μm to 1 μm , energy band gap E_g , index of refraction, and some photoconductivity measurements. The E_g at room temperature and 78°K was found to be 1.78 and 2.09 eV, respectively, and the complex index of refraction at 1 μm wavelength is $N = 3.13 - i(3.2 \times 10^{-5})$.

1. INTRODUCTION

BiI_3 , with an energy gap of ~ 2.00 eV at room temperature^{1,2} is relatively little known and its methods of growth have not yet been reported. Crystallographically, it seems to have two polytypes but the stable form is rhombohedral having a unit cell in the hexagonal lattice of $a = 7.5 \text{ \AA}$ and $c = 20.7 \text{ \AA}$ crystal³ within the space group $C_{3i}^2 - R3$. The optical properties of BiI_3 have been studied in the USSR, and references 1 and 2 seem to be the most recent publication on its physical properties. The compound is also known as a photoconductor.^{1,4} Its melting point is 407.7°C ⁵ and its extrapolated boiling point is 542°C .^{6,7}

This paper will describe: 1) vapor-phase purification and growth, and 2) characterization of the grown BiI_3 crystals.

2. VAPOR-PHASE PURIFICATION AND GROWTH OF BiI_3

The starting Baker reagent BiI_3 powder has been evacuated in a quartz ampoule to about 10^{-5} torr and introduced in a two-zone furnace where the upper temperature is 420°C and the lower temperature is 300°C . Shiny metallic looking platelets of BiI_3 perpendicular to the hexagonal "c" axis are grown from a first sublimation brown-colored residue of unevaporated BiOI is left behind. The BiOI is probably formed as a result of the hydrolysis of BiI_3 , so that $(\text{BiI}_3)_v + (\text{H}_2\text{O})_v = (\text{BiOI})_s + (2\text{HI})_v$. The emission spectrographic analysis of raw and purified material is shown in Table 1.

Table 1. Spectrochemical analysis of BiI_3 crystals in ppm

	Mg	Si	Ca	Other Elements
Amorphous Raw Material	2.60	29	<2.00	Not Detected
First Sublimation	1.50	<1.00	<2.00	Not Detected
Fourth Sublimation			Not Detected	

Crystals of BiI_3 , after four or five cycles of purification, were introduced in quartz ampoules of 15-mm diameter and evacuated to 10^{-5} torr. The ampoule is placed in a two-temperature-zone furnace where the source is at 380

to 400°C and the cold end of the ampoule in the temperature gradient is at 320 to 350°C, as shown in Fig. 1. A boule is obtained after 48 hours which is polycrystalline at the colder end, but at the hot end gradually becomes single crystalline by a self-seeding procedure. The self seeding is interpreted as stemming from the disappearance of the smaller grain by a c-oriented seed grain whose growth prevails, since c is the easy axis of growth. A typical boule is shown in Fig. 2. The single-crystal boule can be easily cleaved perpendicular to the "c" axis. Source growth experiments were also performed by using a seed crystal of a previously grown boule, allowing the growth of single crystalline boules of 50-mm long and 13-mm diameter.

3. CHARACTERIZATION OF THE BiI_3 CRYSTALS

A twice purified, vapor grown crystal of BiI_3 cleaved from a larger boule has been studied by: 1) x-ray diffraction, 2) optical transmission and optical reflection, and 3) gamma-ray detection.

3.1 X-Ray Studies

Both Laue back-reflection and x-ray diffractometer methods were used. The sample was mounted for the Laue studies, so that the pinhole beam was perpendicular to the flat face. A back reflection Laue study was then made using the white radiation from a copper x-ray target. The sample-to-film distance was 30 mm. The beam diameter impinging on the sample was 1-2 mm in diameter. Severe imperfections and severe twinning show up in this Laue study. A high level of strain, which may be due to the cleavage operation, is present in the wafer causing diffuse streaks to appear. As considerable imperfection was observed in the Laue study, the sample was also scanned in the x-ray diffractometer to indicate whether crystallites showing other orientations were present. The signal was obtained for this study covering an entire diameter of the wafer, indicating that the wafer is oriented with the "c" axis perpendicular to the wafer face. The diffractometer study confirms that [0001] orientation occurs completely across the crystal. Additional minor peaks indicate that a few small crystallites showing other orientations are present. Unidentified peaks also occur which most likely represent Laue reflections.

3.2 Optical Properties

Our studies of the electro-optical properties of the BiI_3 crystals involve the optical absorption studies between 0.6 and 50 μm , from which the energy gap E_g and the complex index of refraction could be evaluated.

Energy band gap measurements have been made at two temperatures on single BiI_3 crystals cleaved perpendicular to the crystallographic C_3 axis (hexagonal "c" axis). The results are shown in Table 2 below and compared with values published by V.I. Vashchenko and V.B. Timofeev² for the same crystallographic plane.

Table 2. Energy gap, E_g , in eV as a function of the temperature $T(^{\circ}\text{K})$ for BiI_3 crystals

$T(^{\circ}\text{K})$	E_g Present Work	E_g Reference 2
293	1.78	1.73
85	--	1.93
78	2.04	--

We were unable to detect any absorption at 11.9 μm as reported by the above authors.² We did, however, observe absorption at 40 μm , as may be seen in the composite graph in Fig. 3, which shows the transmission perpendicular to the cleaved plane for two wavelength ranges: 0.6 to 1.5 μm and 2.5 to 50 μm . The oscillations on the graph are caused by interfering multiple reflections from the two surfaces of the crystal which form a etalon.

M.P. Lisitsa⁸ has developed formulas for the calculation of the complex index of refraction which account for multiple internal reflections. We have used these formulae to calculate the complex index at 1 μm associated with the wavelength of neodymium-doped YAG lasers.

We evaluate the complex index of refraction

$$N = n - ik$$

where n and k are the real and imaginary parts of the complex index with

$$n = \frac{1 + R + \sqrt{4R - (1-R)^2 k^2}}{1 - R}$$

$$k = \frac{\lambda}{8\pi d} \ln \frac{R(R[\eta-2] + 1)}{\eta - R}$$

$$R = \frac{D^2 - \eta^2 + 2\eta + 1 - \sqrt{(D^2 - \eta^2 + 2\eta + 1)^2 - 4\eta(2-\eta)}}{2(2-\eta)} \quad (* \text{ see footnote})$$

where R is the coefficient of surface reflection, d is the crystal layer thickness, D and η are the measured transmission and reflection coefficients.

In our studies the relationships $D = 0.56$, $\eta = 0.41$, and $d = 7.6 \times 10^{-3}$ cm give a complex index refraction of

$$N = 3.13 - i(3.2 \times 10^{-5})$$

3.3 Gamma-Ray Detection

Aquadag contacts were placed on undamaged sections of a cleaved [0001] slice and of a non-purified BiI_3 crystal, which allowed measurement of the current voltage characteristics in the dark. Currents on the order of microamps at voltages below 100 V were observed. When the crystal was exposed to light, it showed some increase in current due to photoconductivity, but not very much (factors of two with a 100-V bulb one foot away).

One cleaved [0001] slice of a purified ingot of BiI_3 (four times resublimed) has been subsequently tested. Instead of Aquadag contacts, evaporated gold was used. Currents were considerably smaller, on the order of nanoamps with voltages up to several hundred volts. This value of current is what one would expect, roughly, from the band gap of the material in conduction. Photoconductivity was quite marked when the box was open to room lighting.

*We note in the English translation of Lisitsa's paper⁸ that his expression for R , the solution of a quadratic equation, should use the minus sign (rather than the plus sign) in front of the square root. If the plus sign is used the result is the physically impossible situation where R is greater than η and the total reflected and transmitted radiation will exceed 100 percent.

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LIST OF FIGURE CAPTIONS

Figure 1: Temperature profile of furnace

Figure 2: Boule of BiI_3

Figure 3: Optical transmission of BiI_3 between 0.6 and 1.5 μm and 2.5 to 50 μm

TRANSMISSION VERSUS WAVELENGTH OF BiI_3 CRYSTALS

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