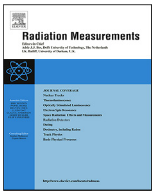
Radiation Measurements 74 (2015) 47–52

Contents lists available at ScienceDirect

Radiation Measurements

journal homepage: www.elsevier.com/locate/radmeas



Growth, fabrication, and testing of bismuth tri-iodide semiconductor radiation detectors

Sasmit S. Gokhale [a, *], Hyuksu Han [b], James E. Baciak [a], Juan C. Nino [b], Kelly A. Jordan [a]

[a] *Nuclear Engineering Program at the Department of Materials Science and Engineering, 100 Rhines Hall, University of Florida, Gainesville, FL 32611, USA*
[b] *Department of Materials Science and Engineering, 100 Rhines Hall, University of Florida, Gainesville, FL 32611, USA*

HIGHLIGHTS

- Ultrapure BiI_3 crystal was grown by the modified vertical Bridgman technique.
- BiI_3 radiation detectors were fabricated and tested.
- The ultrapure detectors showed superior electrical characteristics.
- Radiation response was measured by recording an α-spectrum at room temperature.
- Electron mobility was estimated.

ARTICLE INFO

Article history:
Received 14 April 2014
Received in revised form
6 December 2014
Accepted 27 January 2015
Available online 28 January 2015

Keywords:
Room temperature semiconductor detectors
Semiconductor materials
Radiation spectrometers

ABSTRACT

Bismuth tri-iodide (BiI_3) is an attractive material for high energy resolution radiation detectors. For the purpose of this research, detectors were fabricated using single crystals grown from ultra-pure BiI_3 powder; synthesized by the Physical Vapor Transport (PVT) technique. This technique yielded powder with total impurity level of 7.9 ppm. Efforts were also made to purify commercial BiI_3 powder using a custom-built Traveling Zone Refining (TZR) system. Initial trial runs were successful in reducing the total impurity level of the commercial powder from 200 ppm to less than 50 ppm. Using the modified vertical Bridgman technique and a customized sharp tip ampoule, a large BiI_3 single crystal was grown. The crystal had a surface area of 2.2 cm^2 and a thickness of 0.8 cm, which corresponds to a volume of 1.78 cm^3. Radiation detectors were fabricated and then tested by measuring their electrical characteristics and radiation response. An alpha particle spectrum (using a ^{241}Am α-source) was recorded at room temperature with a BiI_3 detector 0.09 cm thick and with a surface area of 0.16 cm^2. The electron mobility was estimated to be 433 ± 79 cm^2/V.

1. Introduction

Gamma-ray spectroscopy is of interest for a number of applications including, astronomy, medical imaging, reactor engineering, and nuclear security. These applications require detectors with high efficiency and excellent energy resolution. Detectors fabricated from wide band-gap semiconductor materials possess the properties necessary for high detection efficiency and energy resolution; in addition, they can also operate at room temperature without the need for cryogenic cooling (Schlesinger and James, 1995). Over the years a number of compound semiconductors such as cadmium zinc telluride (CdZnTe) (McGregor and Hermon, 1997), cadmium telluride (CdTe) (Shoji et al., 1992), and thallium bromide (TlBr) (Hitomi et al., 2001) have been investigated and successfully applied for room temperature radiation detection.

Iodine based semiconductors such as mercuric iodide (HgI_2) and lead iodide (PbI_2) possess all of the necessary properties required for room temperature gamma-ray spectroscopy and they have been successfully used as radiation detectors. There are however some material and growth issues with both HgI_2 and PbI_2 (Lintereur et al., 2008) and as a result these materials have not gained much popularity. BiI_3 is a semiconductor material, which has properties similar to HgI_2 and PbI_2, but it does not share their major limitations (Dmitriev et al., 1999). BiI_3 has high effective atomic number (since $Z_{Bi} = 83$ and $Z_I = 53$) and high density (5.78 g/cm^3) and thus has a very good photon stopping power (Matsumoto et al., 2002).

---

[*] Corresponding author.
E-mail address: sasmitg@ufl.edu (S.S. Gokhale).

http://dx.doi.org/10.1016/j.radmeas.2015.01.015
1350-4487/

The large band-gap energy (1.67 eV (Qiu et al., 2013)) of BiI_3 will allow it to function as a room temperature radiation detector without any cooling mechanism. HgI_2, PbI_2, and BiI_3 all have a layered crystal structure with weak van der Waals bonding between the layers, and therefore the crystals are mechanically soft and cleave easily (Fornaro et al., 2006). Unlike HgI_2, BiI_3 does not undergo phase transition since it has only one phase (rhombohedral (Yorikawa and Muramatsu, 2008)) which simplifies its crystal growth; furthermore, it is more robust and less toxic than PbI_2 (Hostettler and Schwarzenbach, 2005), (Schlesinger and James, 1995). MCNP calculations have also predicted that BiI_3 has a much higher (by a factor of 2–3) photopeak efficiency than CdZnTe (Lintereur et al., 2008). All of these properties have made BiI_3 an attractive option for further development as a room temperature radiation detector.

2. BiI_3 ultra-pure powder synthesis

The ultra-pure (6N) powder used for growing BiI_3 single crystals was synthesized by the physical vapor transport (PVT) technique. Commercially available lumps of ultra-pure metal bases Bi and I_2 were used for the powder synthesis. The reaction between bismuth and iodine vapors is facilitated by the flow of Argon (Ar) gas through a quartz tube in a two zone tube furnace. A boat with a lump of iodine is placed near one end of the quartz tube in a heating zone at 150 °C to avoid BiI_3 deposition on the quartz boat. The boat with a lump of bismuth is placed near the center of the quartz tube in a zone heated to 400 °C. The synthesized BiI_3 powder is collected on a Teflon® sheet at the other end of the tube, which is maintained at a temperature close to room temperature. The reaction apparatus and the tube furnace can be seen in Fig. 1.

The impurity analysis was carried out by ICP-AES (inductively coupled plasma – atomic emission spectroscopy). BiI_3 powder was dissolved in 10% trace metal grade HCl solution with a concentration of 10 mg/ml. The results of the analysis are summarized in Table 1. Total impurity level of the PVT synthesized powder was measured to be approximately 7.9 ppm. Some of the elements probed had concentrations below the detection limit of the ICP-AES, and thus were noted as ND (Not Detected) in the table. The total impurity level indicates the concentration of the elements that can be probed by ICP-AES only and not all possible impurities.

Table 1
Impurity analysis of PVT synthesized BiI_3 powder.

Element	C. (ppm)	Element	C. (ppm)	Element	C. (ppm)	Element	C. (ppm)
Cu	0.3	Li	ND	Cr	ND	Mo	0.1
Ag	ND	Be	ND	Mn	ND	Cd	0.1
Pb	ND	Mg	1.1	Co	ND	Sb	ND
Ni	ND	Ca	ND	Zn	ND	Tl	ND
Fe	ND	K	ND	As	1.3	B	4.3
Na	ND	Ti	ND	Se	ND	Al	ND
Si	ND	V	ND	Sr	ND	Ba	0.7

Table 2
Impurity analysis of commercially synthesized BiI_3 powder.

Element	C. (ppm)	Element	C. (ppm)	Element	C. (ppm)	Element	C. (ppm)
Cu	ND	Li	ND	Cr	ND	Mo	0.75
Ag	4.47	Be	ND	Mn	ND	Cd	0.1
Pb	ND	Mg	0.58	Co	1.57	Sb	ND
Ni	63.73	Ca	6.59	Zn	ND	Tl	ND
Fe	12.83	K	22.18	As	ND	B	2.36
Na	ND	Ti	0.73	Se	ND	Al	1.03
Si	ND	V	ND	Sr	ND	Ba	ND

The impurity level of the commercially acquired BiI_3 powder manufactured by MV Laboratories (nominal purity 5N) was also measured in order to compare it to that of the PVT synthesized powder. The results of the ICP-AES analysis can be seen in Table 2. As can be seen from the table, the total impurity level of the commercial powder was around 116.92 ppm. High concentrations of metallic impurities, such as Ni (63.73 ppm) and Fe (12.83 ppm), were also detected in the commercial powder.

Efforts were also made to purify commercial BiI_3 powder using a custom built traveling zone refining (TZR) system. In order to purify the BiI_3 powder, it was sealed in an ampoule, which was then mounted into the TZR setup. The TZR setup consists of a band heater, which establishes a narrow molten zone, which is then moved along the length of the ampoule. The moving molten zone causes the impurities to be segregated at one end of the ampoule,

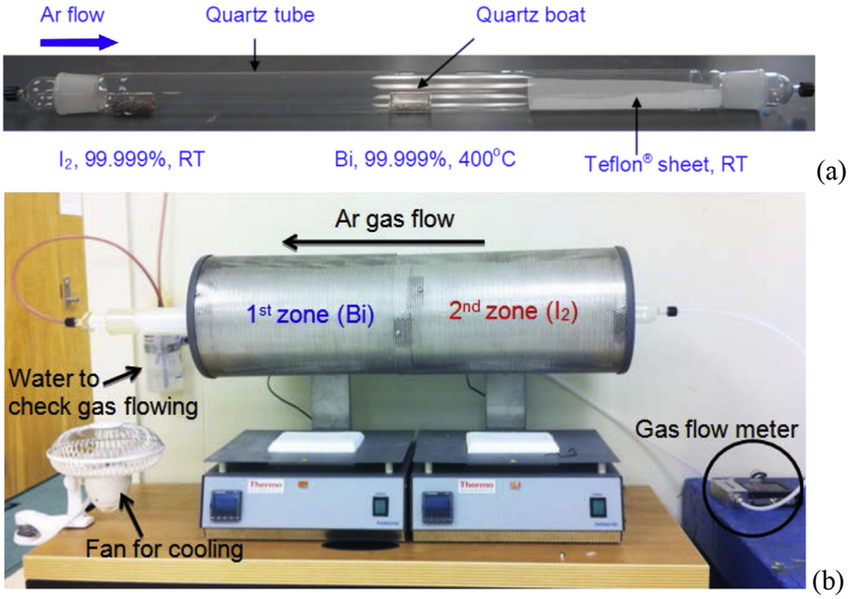


Fig. 1. Reaction apparatus for BiI_3 powder synthesis. (a) Quartz tube, (b) two zone furnace setup.