Journal of Crystal Growth 419 (2015) 143–148

Contents lists available at ScienceDirect

Journal of Crystal Growth

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

Bulk crystal growth, and high-resolution x-ray diffraction results of LiZnP semiconductor material

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ARTICLE INFO

Article history:
Received 1 October 2014
Received in revised form
20 February 2015
Accepted 1 March 2015
Communicated by: A. Burger
Available online 9 March 2015

Keywords:
A1. Radiation
A1. x-ray diffraction
A1. Crystal Structure
A2. Bridgman technique
B1. Lithium compounds
B2. Semiconducting ternary compounds

ABSTRACT

Nowotny–Juza compounds continue to be explored as a candidate for solid-state neutron detectors. Such a device would have greater efficiency, in a compact form, than present day gas-filled ^{3}He and ^{10}BF$_3$ detectors. The ^{6}Li(n,t)^{4}He reaction yields a total Q-value of 4.78 MeV, larger than ^{10}B, an energy easily identified above background radiations. Hence, devices fabricated from semiconducting compounds containing either natural Li (nominally 7.5% ^{6}Li) or enriched ^{6}Li (usually 95% ^{6}Li) may provide a semiconductor material for compact high efficiency neutron detectors. Starting material was synthesized by preparing equimolar portions of Li, Zn, and P sealed under vacuum (10^{-6} Torr) in quartz ampoules lined with boron nitride and subsequently reacted in a compounding furnace [1]. The synthesized material showed signs of high impurity levels from material and electrical property characterizations. A static vacuum sublimation in quartz was performed to help purify the synthesized material [2]. Bulk crystalline samples were grown from the purified material. An ingot 9.6 mm in diameter and 4.0 mm in length was harvested. Individual samples were characterized for crystallinity on a Bruker AXS Inc. D2 CRYSO, energy dispersive x-ray diffractometer, and a Bruker AXS D8 DISCOVER, high-resolution x-ray diffractometer with a 0.004° beam divergence. The (220) orientation was characterized as the main orientation with the D2 CRYSO, and confirmed with the D8 DISCOVER. An out-of-plane high-resolution rocking curve yielded a 0.417° full width at half maximum (FWHM) for the (220) LiZnP. In-plane ordering was confirmed by observation of the (311) orientation, where a rocking curve was collected with a FWHM of 0.294°.

1. Introduction

Nowotny–Juza compounds were originally, and are still today, studied for photonic applications [3–5]. The filled tetrahedral compound class $A^IB^{II}C^V$ materials consist of the III-V-like compounds with lithium interstitials. These materials are desirable for their zincblende cubic crystal structure, and unlike thin-film and doped devices, the concentration of Li atoms is equal to other constituent atoms, as seen in Fig. 1. The zincblende crystal structure is arranged where the group II atom is located at $\tau_1=(0,\ 0,\ 0)a$ where a is the lattice constant, and the group V atom is located at $\tau_2=(1/4,\ 1/4,\ 1/4)a$. The spacious cubic structure allows for lithium atoms to fill the interstitial site at $\tau_3=(1/2,\ 1/2,\ 1/2)a$ as shown in Fig. 1 [6,7]. The filling of these interstitial sites allows for a lithium-loaded semiconducting material. A variety of the ternary compounds have been synthesized in the past, commonly in graphite lined quartz ampoules [8]. Synthesis in a tantalum lined crucible has also been reported [6]. However, bulk growth of these materials has not been reported. The existing material and electrical properties have been reported from samples procured by direct reaction of elemental and/or binary materials. These samples are generally tiny facets extracted from the reaction mixture, and are usually small and extremely difficult to handle and process into devices

Materials containing ^{6}Li, ^{10}B, ^{113}Cd, ^{157}Gd and ^{199}Hg have been considered for solid-state neutron detectors [9–20]. The ^{10}B(n, α)^{7}Li reaction is desirable for the ^{10}B microscopic thermal neutron absorption cross section of 3839 b, but boron-based compounds, such as BP, BN, and BAs have shown limited success, and thus far do not appear promising due to crystal growth and materials preparation problems [17–20]. Thin-film boron devices suffer due to their geometry, where only one reaction product can be absorbed in semiconducting material, therefore producing some signals that can be difficult to distinguish from background and gamma-ray induced events [21]. In addition, because of the reaction product self-absorption, the reactive film thickness is

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http://dx.doi.org/10.1016/j.jcrysgro.2015.03.001
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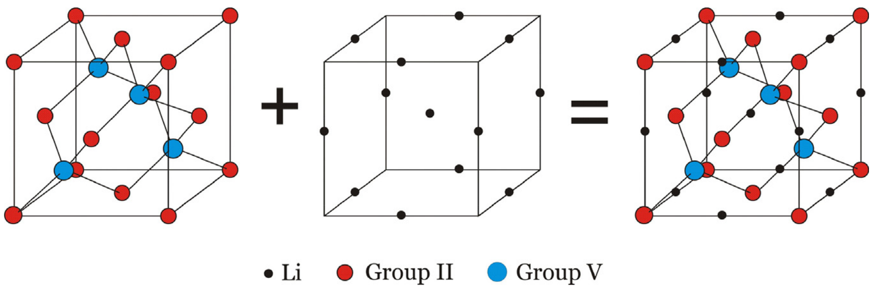

Fig. 1. The cubic crystal structure of $A^{I}B^{II}C^{V}$ compounds.

restricted, and therefore thermal neutron absorption is limited, consequently resulting in a maximum intrinsic detection efficiency of approximately 4.5% [21]. Solid-state detectors containing ^{113}Cd and ^{199}Hg devices also have limited detection efficiency due to the low absorption probability of the prompt gamma-rays that result from $^{113}Cd(n,\gamma)^{114}Cd$ and $^{199}Hg(n,\gamma)^{200}Hg$ reactions [9–12]. The reaction $^{157}Gd(n,\gamma)^{158}Gd$ is desirable for the large ^{157}Gd thermal neutron capture cross section of 240,000 b. Unfortunately, the $^{157}Gd(n,\gamma)^{158}Gd$ reaction yields a spectrum of low energy prompt gamma rays and low energy conversion electrons, all of which are difficult to discern from background radiations [21]. Finally, ^{6}Li has not been explored to the same extent as other thermal neutron absorbers, and has an intrinsic thermal neutron absorption cross section of 940 b. The reaction produces a total Q-value of 4.78 MeV, described by the following reaction,

$$^{6}Li+^{1}_{0}n\rightarrow {}^{3}H(2.73\,MeV)+\alpha(2.05\,MeV). \qquad (1)$$

LiZnP has been reported to have a bandgap of 2.1 eV, ideal for a room-temperature semiconductor device [8]. A Hall mobility of 1–10 $cm^2/V\,s$ was reported by Kuriyama [6]. These known electrical properties make LiZnP and other compounds in the class desirable for compact, high neutron sensitivity, solid-state detectors. Synthesis of Nowotny–Juza materials is not trivial. Lithium is very reactive, and the high-pressures that are developed due to the exothermic reactions that occur during the reaction process often result in containment failure. It was found that making the alloy, Li–Zn, prior to reaction aided the reaction process, and resulted in a much higher ampoule yield [1].In addition, melting temperatures of this class of materials have not been completely characterized [6,8,22]. Reported melting temperatures were not consistent with what was observed in the following study. Unfortunately, the difficulties in the synthesis and handling process limit the available physical and electrical property data [3–8,22,23].

2. Experimental details

Described in the following work is a method developed for the bulk crystal growth process of LiZnP, post processing methods, and the high-resolution XRD characterization.

2.1. *Bulk crystal growth*

LiZnP was synthesized, as described elsewhere, in small batches up to 2.0 g [1]. The synthesized material was purified by a static sublimation process. The process appears to successfully separate the ternary LiZnP material from elemental and binary residual materials that often result from the synthesis process [2]. This purified LiZnP material was subsequently grown into bulk crystals under a high-temperature vertical Bridgman technique.

A 0.5 in. diameter tantalum tube (0.02 in. wall thickness) was cut into a 2.9375 in. long sample containment tube. Tantalum caps were punched, and formed from 0.02 in. thick tantalum sheet. A pyrolytic graphite crucible was custom designed to fit comfortably in the tantalum tube (supplied by Mersen, Inc.). Each of the components were cleaned of oils and contaminants by ultrasonic vibration in a series of solvents namely, isopropanol, acetone and trichloroethylene. The components were loaded into an argon glove box, with minimal oxygen and moisture contamination of less than 0.1%. The bottom cap was welded on the tantalum tube by a Maxstar 150 STL arc welder. The welding torch/stick was fed through the glove box, and the argon environment allowed for the arc plasma to form, and therefore allowed for welding within the box. Purified LiZnP material (1.19 g) was produced, as detailed elsewhere [1,2] was loaded into the pyrolytic graphite crucible, which was loaded into the tantalum vessel. A tantalum cap was welded to the top of the vessel, thereby, making an air-tight containment of LiZnP material and atmospheric pressure argon as shown in Fig. 2.

A bulk crystal was grown in the tantalum vessel contained in a vacuum chamber, equipped with an Omega iR2C series fiber optic thermometer mounted on a two axis rotation stage for alignment purposes. The vacuum chamber was equipped with two feed-throughs connected to an R.D. Mathis LV 400 high-current and low-voltage power source. The tantalum vessel was connected between two electrical connecting oxygen-free plates, referred to as a *copper harness*, depicted in Fig. 3. The copper harness connected to the electrical feed-throughs within a vacuum chamber and these feed-throughs connected to the high-current and low-voltage power source. Continuity was tested to confirm a stable connection outside of the vacuum chamber. The chamber was evacuated, and then purged with ultra-high purity argon at least six times. After the final purge, the chamber pressure was maintained between 300–400 mTorr argon pressure. The current was ramped typically from 0 A to approximately 295–315 A over the course of at least an hour, until the optical thermometer measured approximately 1345 °C at the tantalum surface. Temperature was maintained for at least an hour. The system was then ramped down to room temperature over the following 40 h. The vessel was extracted from the chamber, and opened with a pipe cutter under a pure argon environment. The ingot was harvested, and individual samples were cut from the ingot with a Laser Technology West Ltd. CS400 diamond wire saw while under a constant flow of mineral oil for protection from moisture in the air.

2.2. *x-ray diffraction measurements*

A LiZnP sample was sliced to $4.077 \times 3.518 \times 2.020\ mm^3$, and XRD analysis was performed on one side of the $4.077 \times 3.518\ mm^2$ face. The sample was mounted into a polishing fixture by parafin wax. The sample face was polished with a series of silicon carbide polishing papers ranging from 15.3–2.5 μm grain size, ANSI grit: 600 (P1200), 800 (P2400), and 1200 (P4000) [24,25]. The polished sample was mounted under argon between two Biaxially-oriented polyethylene terephthalate (BoPET) sheets, known as Mylar®, in a