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Static sublimation purification process and characterization of LiZnAs semiconductor material

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ABSTRACT

Refinement of the class $A^IB^{II}C^V$ materials continue 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 $^6Li(n,t)^4He$ reaction yields a total Q value of 4.78 MeV, larger than ^{10}B, and easily identified above background radiations. Hence, devices composed of 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. A sub-branch of the III–V semiconductors, the filled tetrahedral compounds, $A^IB^{II}C^V$, known as Nowotny–Juza compounds, are known for their desirable cubic crystal structure. Starting material was synthesized by equimolar portions of Li, Zn, and As sealed under vacuum (10^{-6} Torr) in quartz ampoules with a boron nitride lining, and reacted in a compounding furnace [1]. The synthesized material showed signs of high impurity levels from material and electrical property characterization. In the present work, a static vacuum sublimation of synthesized LiZnAs loaded in a quartz vessel was performed to help purify the synthesized material. The chemical composition of the *sublimed material* and *remains material* was confirmed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). Lithium was not detected in the *sublimed material*, however, near stoichiometric amounts of each constituent element were found in the *remains material* for LiZnAs. X-ray diffraction phase identification scans of the *remains material* and *sublimed material* were compared, and further indicated the impurity materials were removed from the synthesized materials. The remaining powder post the sublimation process showed characteristics of a higher purity ternary compound.

1. Introduction

A variety of materials have been considered for neutron detectors, including ^{6}Li, ^{10}B, ^{113}Cd, ^{157}Gd, or ^{199}Hg [2–13]. Boron-10 has microscopic thermal neutron absorption cross section of 3839 barns and reacts with a thermal neutron in the $^{10}B(n,\alpha)^7Li$ reaction. Boron compounds including BP, BN, and BAs have shown limited success, and thus far do not appear promising due to crystal growth and materials preparation problems [10–14]. Thin-film coated diode detectors have been studied as a possible alternative, however, they suffer due to their geometry. The detection efficiency is limited, due to only one reaction product that can be absorbed in semiconducting material, thereby, producing some signals that are difficult to distinguish from background events [15]. Additionally, thin film thickness is restricted, depending on the range of the reaction products in the boron material, and therefore thermal neutron absorption is limited, resulting in a maximum intrinsic detection efficiency of approximately 4.5% [15]. Gamma-ray emitting materials, such as ^{113}Cd and ^{199}Hg, have been considered for solid-state detectors. These devices also have limited detection efficiency due to the low absorption probability of the prompt gamma-rays that result from the reactions $^{113}Cd(n,\gamma)^{114}Cd$ and $^{199}Hg(n,\gamma)^{200}Hg$ reactions [2–5]. Gadolinium-157 has thermal neutron capture cross section of 259,000 barns and interacts with a thermal neutron by $^{157}Gd(n,\gamma)^{158}Gd$ [16]. Unfortunately, this reaction results in low energy prompt gamma rays and conversion electrons below 220 keV, mostly near 50 keV, which are difficult to discern from background radiations [15]. Unlike other neutron absorbers, ^{6}Li has not been explored to the same extent and has an intrinsic thermal neutron absorption cross section of 940 barns. ^{6}Li reacts with a thermal

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neutron, resulting in a triton of 2.73 MeV and alpha particle of 2.05 MeV, as shown in the following,

$$^{6}\mathrm{Li}+{}^{1}_{0}n\rightarrow{}^{3}\mathrm{H}(2.73\mathrm{M\ eV})+\alpha(2.05\mathrm{M\ eV}).$$

Nowotny–Juza compounds were originally studied for photonic applications, and recently have been considered for Li-ion batteries [17–20]. Shown in Fig. 1 is the $A^{I}B^{II}C^{V}$ zincblende crystal lattice. The arrangement of atoms is unique where the group II atom is located at $\tau_1=(0,0,0)a$ where a is the lattice constant. The group V atom is located at $\tau_2=(1/4,1/4,1/4)a$ and the lithium atoms fill the interstitial site at $\tau_3=(1/2,1/2,1/2)a$ [21]. These materials are desirable for their zincblende cubic crystal structure and high lithium content where, unlike thin-film and doped devices, the concentration of Li atoms is equal to other constituent atoms as shown in Fig. 1. Challenges in synthesis, purification, crystal growth, and handling, unfortunately limit the available physical and electrical property data [17,18,21–25]. The following study addresses the processes that are necessary for synthesizing phase pure LiZnAs material in the powder form. The powders serve as important starting materials necessary for growing high-quality LiZnAs crystals, that are necessary for making semiconductor based neutron detectors.

LiZnAs material was synthesized in sealed, crucible lined quartz ampoules [1,26]. It was noticed that not all synthesis processes yielded high quality material. Some material harvested from the synthesis vessel had observable unreacted portions included in the bulk, and secondary phases were observed in x-ray diffraction phase identification scans as described previously [1]. A multi-step synthesis was performed to yield the highest purity product, although unreacted elemental and binary materials were likely included in the synthesized material [1]. Nowotny–Juza compounds are hygroscopic, thereby, making handling quite difficult. Also, molten lithium reacts with quartz to make lithium silicates, which also narrows available purification techniques [27]. Typical non-solution based purification methods consist of: 1) dynamic vacuum sublimation 2) static vacuum sublimation 3) vacuum distillation, and 4) zone refining. Vacuum distillation is typically performed on elemental materials, or compounds, that do not sublime before becoming molten [28,29]. LiZnAs melts slightly above 1200 °C, and sublimes before becoming molten, therefore a distillation method is not appropriate. Additionally, due to the high melting temperature, traditional zone refining is not a trivial process. A static vacuum sublimation was chosen over dynamic vacuum sublimation due to little concern of $A^{I}B^{II}C^{V}$ material exposure to the atmosphere in the handling process. Sublimation is known to be a clean and effective method to purify elemental and compounded materials [30–32]. Synthesized ternary material was processed through a static vacuum sublimation that successfully reduced the material impurity level.

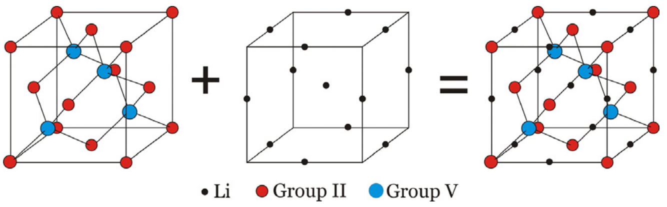

Fig. 1. The Nowotny–Juza filled tetrahedral zincblende cubic crystal structure.

2. Experimental details

The following section entails the sublimation process of LiZnAs, and the ICP-OES and XRD characterization that help verify the process results.

2.1. Sublimation process

LiZnAs was synthesized by the same method described elsewhere [1]. Afterwards, while inside a glove box backfilled with Ar (<5 ppm oxygen, <2 ppm moisture), approximately 5.0 g of LiZnAs was added to a boron nitride crucible boat, and subsequently placed at one end of a clean thick-walled (>2.5 mm) quartz ampoule. A temporary vacuum seal was placed over the open end of the ampoule, and the ampoule was moved to an ampoule sealing station, where the ampoule open end was attached to a pumping station. The ampoule was then heated to remove any residual moisture while under vacuum. When the ampoule vacuum reached approximately 9.8×10^{-6} Torr, it was sealed using a H_2–O_2 torch.

The sealed ampoule was placed into a three zone furnace, where the ampoule was mounted in the furnace so that the *cold* end of the ampoule extended to the edge of the furnace as shown in Fig. 2. All three zones were ramped to 550 °C at 3 °C/min and held at temperature for at least an hour. Two adjacent zones controlling the material temperature were ramped to 720 °C at 3 °C/min, and the third, cooler zone remained at 550 °C. Temperature was maintained for approximately 24 h, or until no further material transport was observed.

Once the process was complete, samples from each end of the ampoule were collected, one from the *sublimed material* and one from the *remains material* still in the boat, as shown in Fig. 3. These samples were analyzed by elemental analysis on a Varian 720-ES Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) instrument. This method uses simultaneous optical systems, and axial or radial viewing of the plasma to measure characteristic emission spectra by optical spectroscopy. Note that this particular elemental analysis has been known to have up to 10% relative standard deviation about the measured elemental weight [33]. However, with careful preparation of the calibration standards, and samples, this relative error can be reduced.

Phase identification x-ray diffraction scans were carried out using a Bragg Brentano Geometry on a Bruker D8 Advance Diffractometer, equipped with a Cu source, for each of the *sublimed material*, and *remains material* samples harvested from the

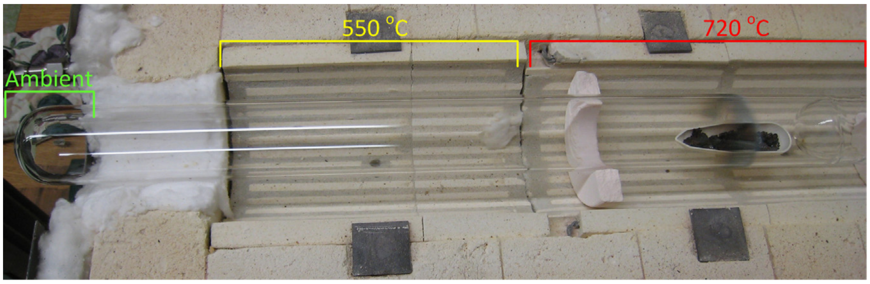

Fig. 2. Ampoule prepared for static sublimation process.