Static Sublimation Purification Process and Characterization of LiZnAs Semiconductor Material

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Keywords: A1. Purification; B1. Lithium Compounds; A1. Radiation; B2. Semiconducting ternary compounds; A1. X-ray diffraction

ABSTRACT

Refinement of the class $A^I B^II C^V$ 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 ^3He and $^{10}\text{BF}_3$ detectors. The $^6\text{Li}(n,t)^4\text{He}$ 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% ^6Li) or enriched ^6Li (usually 95% ^6Li) may provide a semiconductor material for compact high efficiency neutron detectors. A sub-branch of the III-V semiconductors, the filled tetrahedral compounds, $A^I B^II C^V$, 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.

INTRODUCTION

A variety of materials have been considered for neutron detectors, including ${}^6\text{Li}$, ${}^{10}\text{B}$, ${}^{113}\text{Cd}$, ${}^{157}\text{Gd}$, or ${}^{199}\text{Hg}$ [2-13]. Boron-10 has microscopic thermal neutron absorption cross section of 3839 barns and reacts with a thermal neutron in the ${}^{10}\text{B}(n,\alpha){}^7\text{Li}$ 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 ${}^{113}\text{Cd}$ and ${}^{199}\text{Hg}$, 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 ${}^{113}\text{Cd}(n,\gamma){}^{114}\text{Cd}$ and ${}^{199}\text{Hg}(n,\gamma){}^{200}\text{Hg}$ reactions [2-5]. Gadolinium-157 has thermal neutron capture cross section of 259,000 barns and interacts with a thermal neutron by ${}^{157}\text{Gd}(n,\gamma){}^{158}\text{Gd}$ [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, ${}^6\text{Li}$ has not been explored to the same extent and has an intrinsic thermal neutron absorption cross section of 940 barns. ${}^6\text{Li}$ reacts with a thermal neutron, resulting in a triton of 2.73 MeV and alpha particle of 2.05 MeV, as shown in the following,

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 $\text{A}^{\text{I}}\text{B}^{\text{II}}\text{C}^{\text{V}}$ 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 sublimates 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^IB^{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.

EXPERIMENTAL DETAILS

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

I. 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 grams of LiZnAs was added to a boron nitride crucible boat, and subsequently placed at one end of a clean thick-walled (>2.5mm) 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 H₂-O₂ 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 hours, 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 respective side of the purification ampoule. Samples were ground into a fine powder, placed into a sample holder, and sealed under argon by a layer of mylar to prevent air exposure. A phase identification scan was collected for each sample, and were compared with theoretical phase locations calculated with PowderCell 2.4 [34], and with data reported in the literature [18, 35].

II. ICP-OES process

Standard solutions of varying concentrations (0, 1, 3, and 5 mg/L – Li; 0, 15, 30, 50, and 70 mg/L – Zn; 0, 15, 30, 50 and 70 mg/L – As) in water were prepared, and measured on a Varian 720-ES ICP-OES instrument to establish concentration curves. Percent deviation, or error, from the expected concentration of each standard solution was determined by the instrument, the results of which are listed in Table 1. LiZnAs *remains material* and *sublimed material* were prepared for ICP-OES analysis. Each 100mg sample was loaded into a Pyrex sample container under argon, and sealed with Parafilm[®] to reduce air exposure when removed from the glove box. In a fume hood, the Parafilm[®] was removed, and 10mL of freshly prepared aqua regia (1:4 volume HNO₃/HCl) was quickly added to each sample. The *remains* side of LiZnAs purification produced a noticeable reaction that produced a black vapor with the addition of aqua regia. The addition of aqua regia to the *deposition* side did not produce a noticeable reaction. The digestion was allowed to continue overnight.

Most of the material was completely dissolved in each sample vial after a 24 hour period. To ensure dissolution of the remaining material, each vial was heated on a digestion block at 75°C for 30 min, 100°C for 30 min, 110°C for 30 min, and 140°C until the acid reduced to approximately 2.0mL [36]. Each solution was then removed from the digestion block and each increased to a 50 mL by adding a 0.1% HNO₃ solution. Each 50mL solution was then filtered through a Whatman[®] no. 42 filter paper. A 2.5 mL sample from each filtrate was diluted to 50mL, each resulting in a solution possessing less than 100 mg/L of each element of interest. Unfortunately, some sample solutions still exceeded detection limits of the ICP-OES instrument, thereby, requiring further dilution by 25% or 50% until a suitable dilution was obtained. At least two measurements were collected for each sample.

The analysis results are listed in Table 2. The percent result of each constituent element was determined based on the instrument analysis of the concentration of the particular element, and the total amount of material originally weighed for analysis. The elemental percent concentrations were then converted to molar concentration using each element's molar mass. The analysis percent error, and molar concentration standard error were determined based on the deviation from the average of the two measurements for each sample.

RESULTS AND DISCUSSION

Static vacuum sublimation of the in-house synthesized powders and chunks of LiZnAs appeared to produce a higher purity ternary material. The ICP-OES results are listed in Table 1 for a purified LiZnAs sample as collected on a Varian 720-ES ICP-OES. Li was not detected in the *sublimed material* sample; however, and the *remains material* was found to have the stoichiometric ratios expected for A^IB^{II}C^V materials, as listed in Table 2. The total weight percent of the sample equaled 89.1 ± 4.0%. Although it is expected to observe an elemental total

of 100%, the standard error associated with the measured total is often larger when including the error associated with the concentration curves. Shown in Table 1 are standard errors up to 8.493% for the 30mg/L Zn solution. The standard error from the slope of the concentration curve was included in quadrature for determination of the final standard error.

The elemental percent concentrations were converted to molar concentration from the molar mass of each element, where it is observed that each molar mass is approximately equal. Arsenic had a slightly lower molar concentration than Li and Zn. The concentration curve standard error for As was determined to be 1.222% for the 20 mg/L standard solution. This relatively high error may suggest the error associated with the As analysis may be slightly higher than the other measurements. Nevertheless, this result is further indication that impurities (binaries, unreacted elemental components) were transferred out of the in-house synthesized material during the sublimation process, leaving a much purer ternary material.

The theoretical phase identification for LiZnAs can be seen in Fig. 4, as calculated using PowderCell 2.4 [34]. The x-ray diffraction phase identification of LiZnAs purification *sublimed material* is shown in Fig. 5, where an array of peaks is observed, many that match nicely with experimental data by Nowotny for LiZnAs [18]. However, the same *sublimed material* phase scan was compared to cubic Zn₃As₂ data collected by Banus [35] (see Fig. 5), where many peaks also match the reported data. Further evidence that Zn₃As₂ was sublimed out of the raw synthesized material can be found by careful examination of the ICP-OES results. Zinc arsenide has a stoichiometric Zn to As ratio of 1.5, and the ratio of Zn to As, as listed in Table 2, is 0.92. These ratios are not consistent, but with an abundance of elemental arsenic mixed amongst the impurities, it is suspected that cubic Zn₃As₂ was formed and is present as an impurity.

The *remains material* phase identification, shown in Fig. 6, shows identifiable peaks, all of which match well with literature in terms of theoretical peak positions as shown in Fig. 4. No contamination peaks were observed here compared to the raw synthesized material which showed many unidentifiable peaks as described elsewhere [1]. A lattice constant was determined using TOPAS (Bruker AXS Inc.). The Whole Pattern decomposition approach was used [37]. Refinement of the *remains material* phase identification data yielded a lattice constant of 5.901 ± 0.002 Å, which is consistent with data reported from raw synthesized (unpurified) material [1].

CONCLUSIONS

Nowotny-Juza compounds were synthesized in-house into powder and chunks, and purified by static sublimation. The ICP-OES indicate the higher vapor pressure binary and elemental materials can be removed from the synthesized material, reducing the impurity level, while retaining the 1:1:1 stoichiometric ratio between constituent elements. The purification material x-ray diffraction studies also indicate that impurities were removed. All prominent phase peaks were accounted for by experimental literature phase locations, or by theoretical phase location. A higher grade material was produced that will be used to grow crystalline ingots that can be processed into devices. Finally, electrical properties (resistivity, electron mobility) and neutron sensitivity will be characterized from these devices.

• Li • Group II • Group V

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

Fig. 2. Ampoule prepared for static sublimation process.

Fig. 3. Two ampoules of LiZnAs post static sublimation process (graphite crucibles were used in initial trials as shown here).

Table 1. The standard solution percent errors, or deviations, from the expected concentrations. Negative values indicate the concentration deviation lies below the expected value.

Element	Concentration	% Error
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	(mg/L)	
	0	0
Li	1	5.116
	3	0.554
	5	-0.404
	0	0
Zn	15	7.151
	30	8.493
	50	3.184
	70	-3.513
	0	0
As	10	0.773
	20	1.222
	30	0.328
	40	-0.428

Table 2. The ICP-OES results of LiZnAs post static sublimation collected on a Varian 720-ES.

Sample: Remains (Purified)			Sample: Sublimate (Elemental, binary)		
Analysis	Result (%)	Molar concentration (mol/L)	Analysis	Result (%)	Molar concentration (mol /L)
As	38.9 ± 0.5	0.000535 ± 0.000003	As	55.6 ± 0.4	0.000720 ± 0.000003
Li	5.3 ± 0.7	0.000791 ± 0.000006	Li	n/a	n/a
Zn	44.9 ± 2.8	0.00071 ± 0.00002	Zn	52.2 ± 2.8	0.000774 ± 0.000002
Total	89.1 ± 4.0

Fig. 4. The theoretical Cu x-ray phase identification of a Cubic LiZnAs $F\bar{4}3m$ powder with a lattice constant of $5.939 \pm .002\text{\AA}$ [1]. Peak positions were calculated with PowderCell 2.4 [34].

Fig. 5. LiZnAs *sublimed material* phase identification scan collected on a Bruker AXS D8 ADVANCE equipped with Cu radiation. The circles above peaks are experimental peak locations from lithium zinc arsenide reported by Nowotny [18]. The triangles above peaks are experimental peak locations from cubic zinc arsenide reported by Banus [35].

Fig. 6. LiZnAs *remains material* phase identification scan collected on a Bruker AXS D8 ADVANCE equipped with Cu radiation. Each orientation labeled here matched to the experimental peaks reported by Nowotny [18].

ACKNOWLEDGEMENTS

The authors express gratitude to John Desper, and the Kansas State University Chemistry Department for the use of their Bruker D8 Advance x-ray diffractometer. Work funded in part by the Advanced Materials program DOE – NNSA, grant # DE-FEG52-08NA28766.

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