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Experimental Investigation of Ternary Alloys for Fusion Breeding Blankets

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1. Background

Future fusion power plants based on the deuterium-tritium (DT) fuel cycle will be required to breed the T fuel via neutron reactions with lithium, which will be incorporated in a breeding blanket that surrounds the fusion source. Recent work by LLNL proposed the used of liquid Li as the breeder in an inertial fusion energy (IFE) power plant [1]. Subsequently, an LDRD was initiated to develop alternatives ternary alloy liquid metal breeders that have reduced chemical reactivity with water and air compared to pure Li. Part of the work plan was to experimentally investigate the phase diagrams of ternary alloys. Of particular interest was measurement of the melt temperature, which must be low enough to be compatible with the temperature limits of the steel used in the construction of the chamber and heat transfer system.

2. Objectives of the Experiments

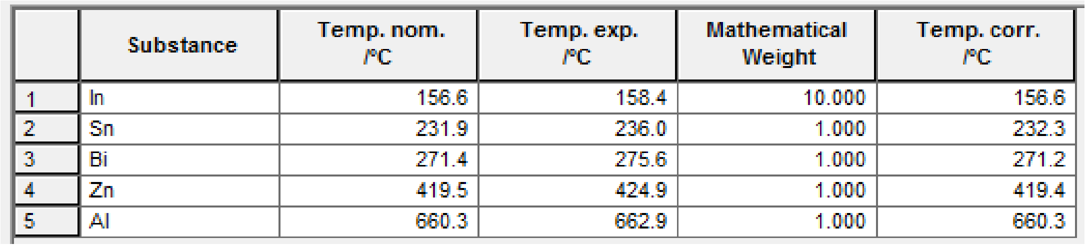
The objectives of this aspect of the research were to 1) measure melt temperature of various compositions of the candidate alloys to determine which were in a range that would be useful for a blanket breeder/coolant, and 2) determine alloy phase information to compare to predicted phase diagrams developed by Turchi [2]. Based on previous scoping work that considered several criteria for candidate breeders, the initial focus was on Li-Sn-Zn alloys.

3. Description of DSC and its Operation

For the determination of alloy melting temperature and any phase change at elevated temperatures, the NETZSCH's STA 449 ***F1** Jupiter*®, High-Temperature Differential Scanning Calorimeter (DSC), was utilized. The DSC thermal instrument measures the temperature change of a sample in a crucible compared to a reference (empty crucible) during programmed heating or cooling. The heat flow is calculated on the basis of this temperature difference curve. When the sample changes state due by melting, evaporation, crystallization, etc., this is detected as a difference in temperature and the DSC curve shows a difference in heat flow. As such, the measurements are sensitive to the difference between the enthalpy versus temperature relation of a sample and the enthalpy versus temperature relation of a standard.

3.1 Calibration of DSC

The enthalpy versus temperature relations of pure metals are well-known and output information from such pure metals from a differential thermal analysis (DTA) is used primarily for calibration. In this project, the temperature calibration of the DSC instrument was carried out using five pure elements whose melting temperatures are well defined: Indium (156.6°C), Tin (231.9°C), Bismuth (271.4°C), Zinc (419.6°C), and Aluminum (660.6°C). The statistic error for overall results was within 2-3 degree C based on systematic temperature sensitivity calibration in this case study. Figure 1 shows the result of the calibration run along with a fitting curve for the temperature sensitivity calibration to be used on this project. All DSC runs performed on this study were conducted at the heating and cooling rate of 20°C/min.



	Substance	Temp. nom. /°C	Temp. exp. /°C	Mathematical Weight	Temp. corr. /°C
1	In	156.6	158.4	10.000	156.6
2	Sn	231.9	236.0	1.000	232.3
3	Bi	271.4	275.6	1.000	271.2
4	Zn	419.5	424.9	1.000	419.4
5	Al	660.3	662.9	1.000	660.3

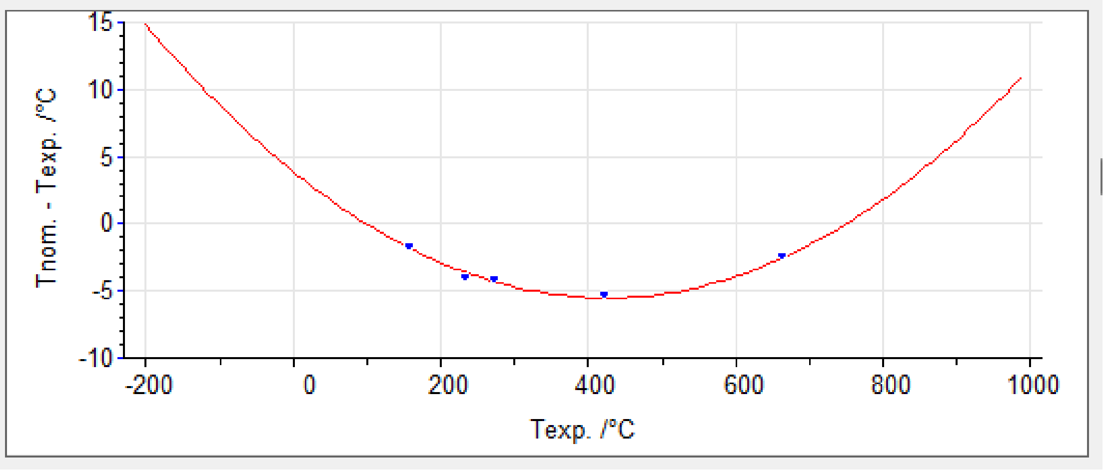


Fig. 1. Results of the DSC calibration run.

4. Sample Preparation

4.1.1 Conventional Approach – Melting in an Inert Glove Box Atmosphere

In an effort to identify new binary/ternary alloys that could exceed the performance metrics of conventional tritium breeding blankets, a series of Li-rich binary and ternary alloys was selected based on neutron studies and predicted ternary phase diagram. The initial selection of Li-rich binary and ternary alloy system is summarized in Table 1 below.

Table 1. Elemental Mix of Initial Alloy Compositions

Sample No.	Composition	Ratio in atomic %	Prep. Method for DSC	Exp. ref. #
1	Li+Sn	80/20	Pre-melted	03
2	Li+Sn	60/40	Elemental mix	04
3	Li+Sn	93.3/6.7	Pre-melted	05
4	Li+Sn	73.3/26.7	Pre-melted	06
5	Li+Sn+Zn	60/20/20	Elemental mix	07

Each sample was weighted first using a precision micro balance according to the atomic ratio, and placed into in high temperature crucible (Tantalum) to form an alloy via the melting process. Each batched sample was heated up under argon atmosphere in the glove box and held at 900 °C for 3 hours with a lid on the crucible. The solidified samples from of the melting pot were separated as a powdery form and/or cored out from the crucible to use for the DSC samples. Figure 2 show the typical of the appearance of the solidified materials upon cooling. It is mostly a very hard shell on the very surface while a bit loosened powdery form at the bottom of the crucible, indicating that complete mixing did not occurred during the melting process.

Fig. 2. Typical ternary alloy appearance prepared using melting approach.

Two out of five samples listed in Table 1 were not pre-melted: the LiSn 60/40 binary and the ternary LiSnZn 60/20/20 ternary. Because the melt was stuck in the crucible, it was not possible to core out a test sample. Therefore, these two samples were prepared by placing each element directly into DSC run crucibles.

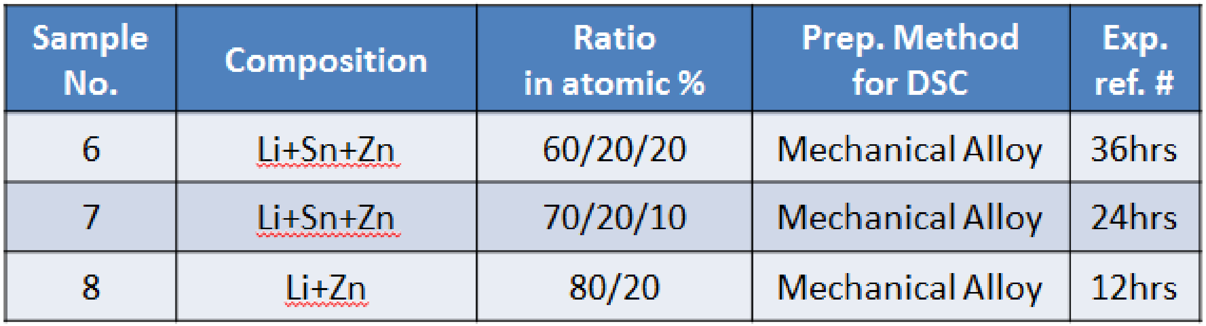
4.2 Different Sample Preparation Approaches and Results

We found that preparation of ternary alloy with Li and/or Zn involved was not viable by the normal technique of melting. The results clearly showed phase separation after the material cooled to room temperature. Hence two other methods of forming alloys with lithium were considered and introduced: 1) mechanical alloying at the room temperature, and 2) using a wet-chemical method (or co-precipitation in solution) in which it is possible to precipitate and recover crystalline alloy materials under certain conditions. Note that the IWS did not allow manual stirring in the melting pot within the high temperature glove box.

4.2.1 Mechanical Alloying

Due to limited time for the alloy development phase of the project, we considered only two ternary systems in LiSnZn systems with atomic ratios of 60/20/20 and other 70/20/10 and one binary system of LiZn at ratio of 80/20.

Table 2. Samples Produced by Mechanical Alloying



Sample No.	Composition	Ratio in atomic %	Prep. Method for DSC	Exp. ref. #
6	Li+Sn+Zn	60/20/20	Mechanical Alloy	36hrs
7	Li+Sn+Zn	70/20/10	Mechanical Alloy	24hrs
8	Li+Zn	80/20	Mechanical Alloy	12hrs

The mechanical alloying route was used to determine if single phase ternary alloy could be prepared. The SPEX high energy ball miller has 12 hardened 316 stainless steel balls, roughly 3/8 inch diameter, inside a machined vial. It was used to perform the mechanical alloying process for up to 36 hours. The resulted material was examined first by XRD to see if it was formed as homogeneous mix and/or as a compound form.

The XRD phase identification results shown in Fig. 3 indicate that the mechanical alloying with lithium and other elements appeared to be a simple process to form a single phase (cubic), which was consistent with the reference alloy indexed LiSnZn on the XRD file. These two samples were intended for use in DSC runs immediately before any contamination via nitrogen and/or oxygen, etc.

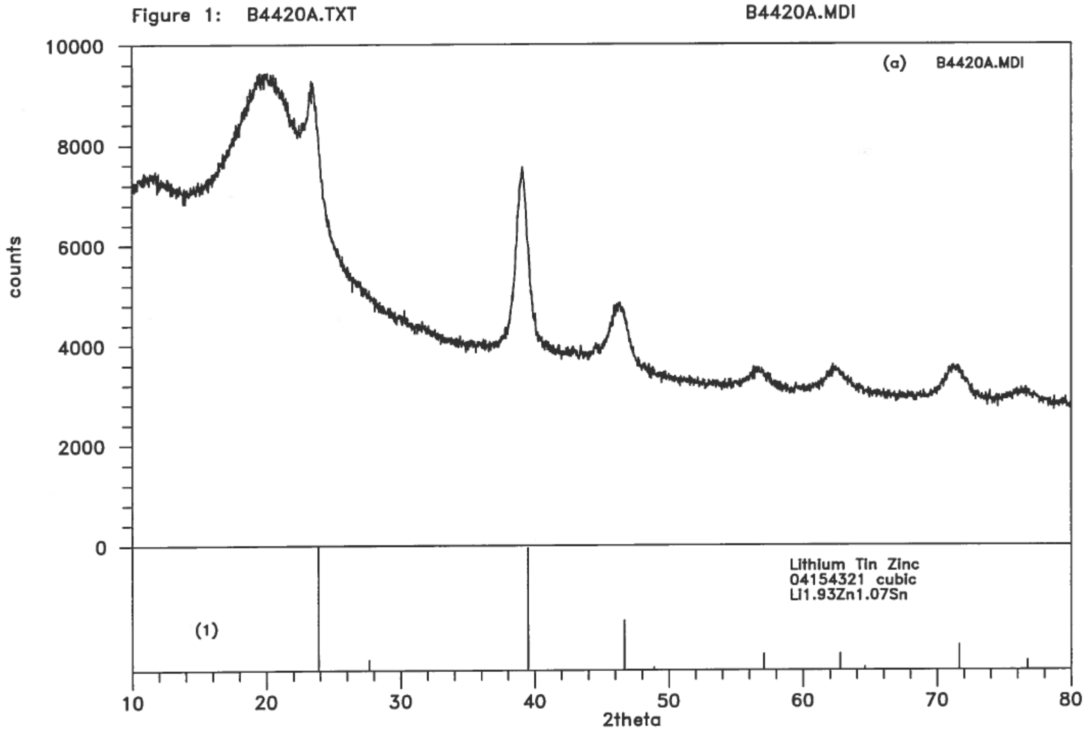


Fig. 3. XRD analysis of LiSnZn alloy.

We investigated the effectiveness of the mechanical alloying process as a function of milling time (using the 60/20/20 LiSnZn) to see if times shorter than the initial 36 hours were possible. The alloying time was controlled at 0, 6, 24 and 36 hours; refer to Table 3 below. To prevent the vials from getting hot, they are cooled using airflow directed from a room air-conditioner. The samples are loaded in an atmosphere-controlled glove box, to prevent interaction with air.

Table 3. LiSnZn 60/20/20 Samples Mechanically Alloyed for Various Durations

X-ray #	Sample ID	Description	Label
X4460	Li6Sn2Zn2	0 hours	(a)
X4462	Li6Sn2Zn2	6 hours	(b)
X4420	Li6Sn2Zn2	24 hours	(c)
X4456d	Li6Sn2Zn2	36 hours	(d)

Figure 4 shows the resultant XRD spectra for the samples (a), (b), (c) and (d). Clearly, as expected, the 0 hour sample indicates the presence of 3 individual phases of Li, Zn and Sn. Upon alloying for just 6 hours, a cubic structure, similar to $Li_{7.72}Sn_{4}Zn_{4.28}$ can be observed. At this time, the peaks are broad because the crystallites are still small. The peaks corresponding to Li, Zn and Sn are no longer observed. Hence, it can be concluded that mechanical alloying is a viable technique to prepare single phase ternary alloy.

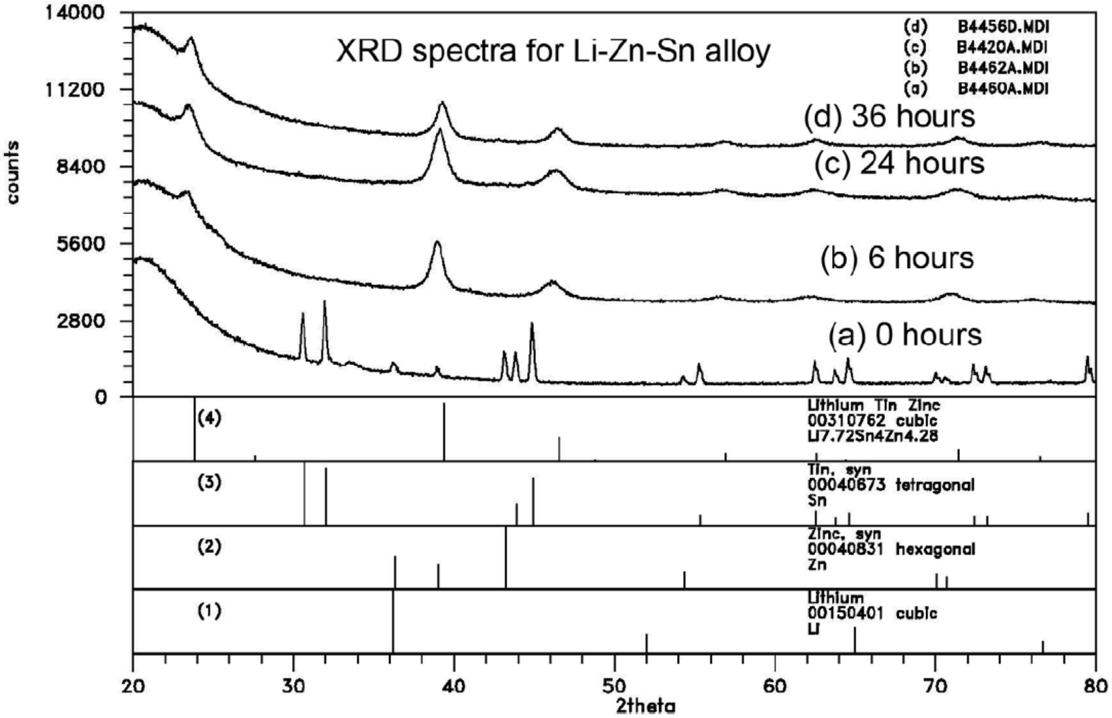
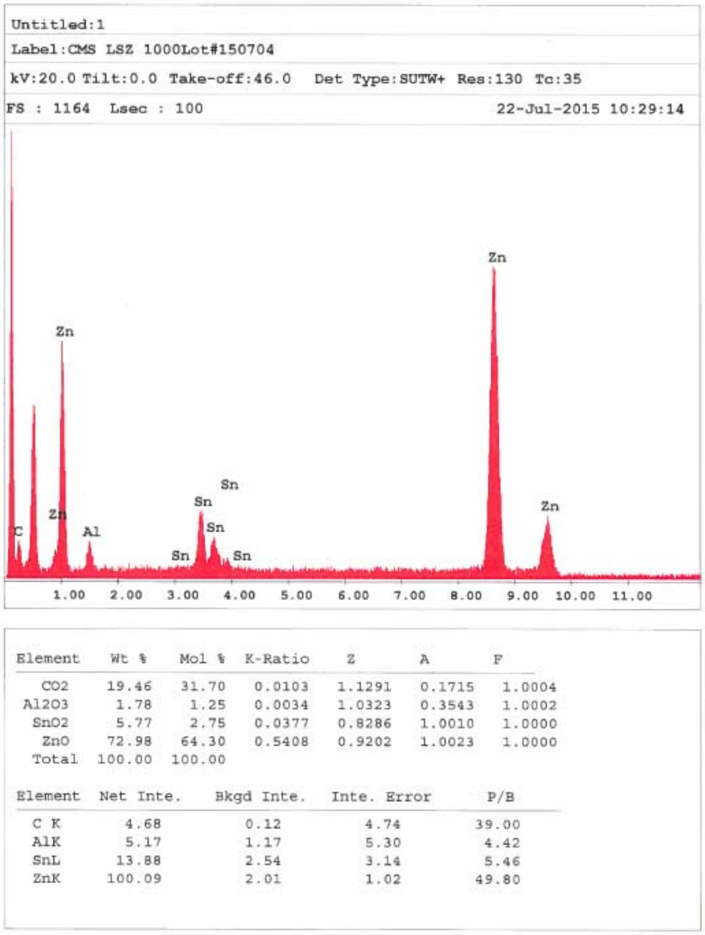


Fig. 4. XRD results for alloys mechanically prepared for 0, 6, 24 and 36 hours.

4.2.2 Co-Precipitation Alloy

As a first trial product, we requested a wet chemical process to be conducted off-site in a company called NanoCMS. This company is well-known for manufacturing proprietary nano-sized ink raw materials via wet chemical methods. They produced a small amount of ternary alloy (LiSnZn 60/20/20) for this LDRD project in powder form. The co-precipitated powder was, according to them, produced by having Lithium carbonate, zinc oxalate and tin oxalate in solution carried down with sodium hydroxide in high temperature; the resulting powder was assumed to be precipitated as in-situ forming a compound. However, in our compositional characterization using SEM chemical analysis, we found that the sample was heavily oxidized (Fig. 5a). We also confirmed a metastable oxide compound rather than metallic compound using X-ray Diffraction (XRD) examination (Fig. 5b). Therefore, no DSC runs were done with the material produce by the precipitation method.



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Label:CMS LSZ 1000Lot#150704

kV:20.0 Tilt:0.0 Take-off:46.0 Det Type:SUTW+ Res:130 Tc:35

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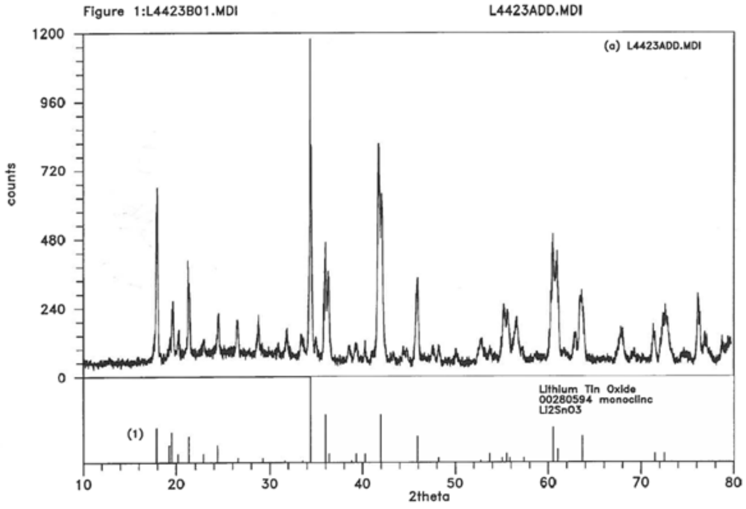
Element	Wt %	Mol %	K-Ratio	Z	A	F
CO2	19.46	31.70	0.0103	1.1291	0.1715	1.0004
Al2O3	1.78	1.25	0.0034	1.0323	0.3543	1.0002
SnO2	5.77	2.75	0.0377	0.8286	1.0010	1.0000
ZnO	72.98	64.30	0.5408	0.9202	1.0023	1.0000
Total	100.00	100.00				

Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
C K	4.68	0.12	4.74	39.00
AlK	5.17	1.17	5.30	4.42
SnL	13.88	2.54	3.14	5.46
ZnK	100.09	2.01	1.02	49.80

(5a)



(5b)

Fig. 5. Analysis of the co-precipitation alloy provided by nanoCMS: a) via SEM and b) via XRD.

5. Alloy Sample Runs (Melt Experiment)

5.1 Binary Results and Comparison to Literature Melt Points

A DSC run result for first binary system is shown in Fig. 6., where the pre-melted LiSn 80/20 batch (sample #1) exhibited a nice and sharp endothermic onset at the temperature of 756°C. This onset point appears to be a phase transformation into the liquid phase which is agreeable with the published phase diagram of LiSn system [3].

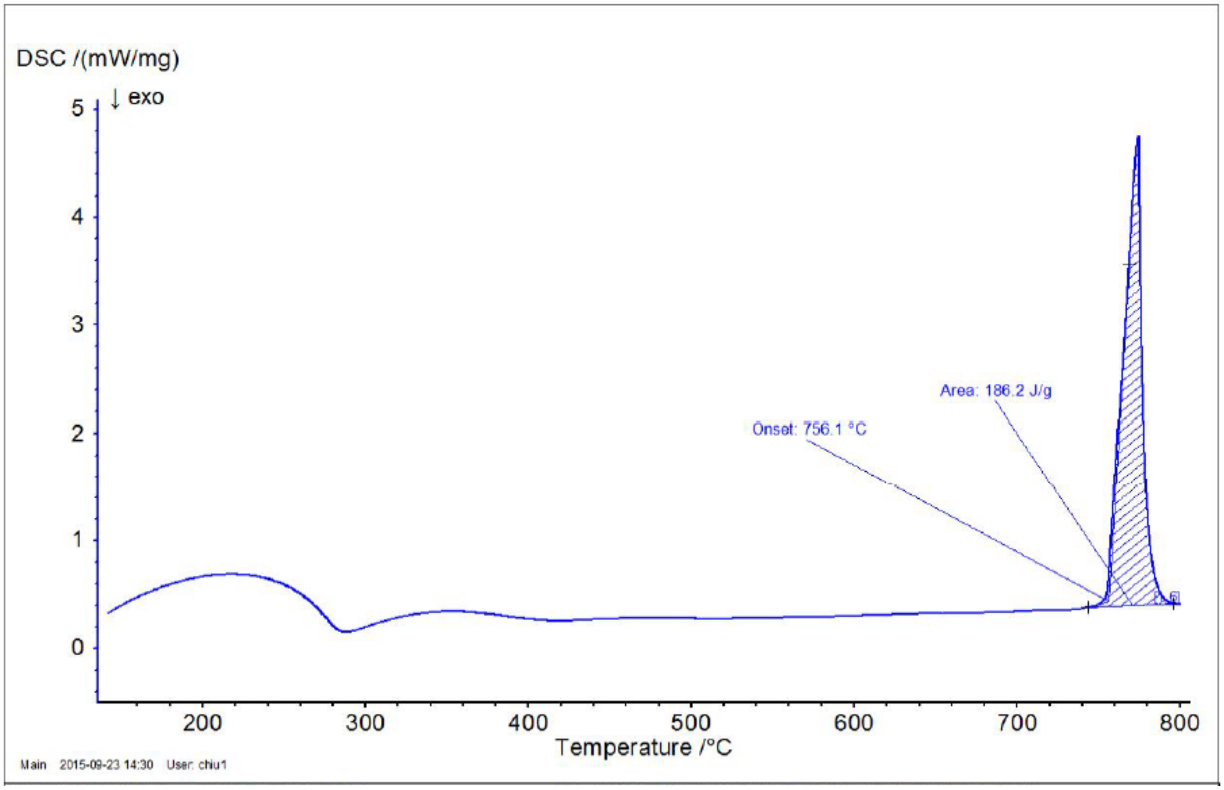


Fig. 6. DCS result for LiSn 80/20.

The addition of 20% Sn to Li-rich region as shown in the phase diagram transforms congruently into the liquid phase at high temperature 772 °C. The onset peak temperature, however does not match those from the data base for the LiSn system (see Fig. 7). Differences in melting temperatures may possibly be compositional shifts due to different atomic compositions which might have occurred in handling since Li is chemically reactive with oxygen and nitrogen in the air and water and is highly corrosive with other compound.

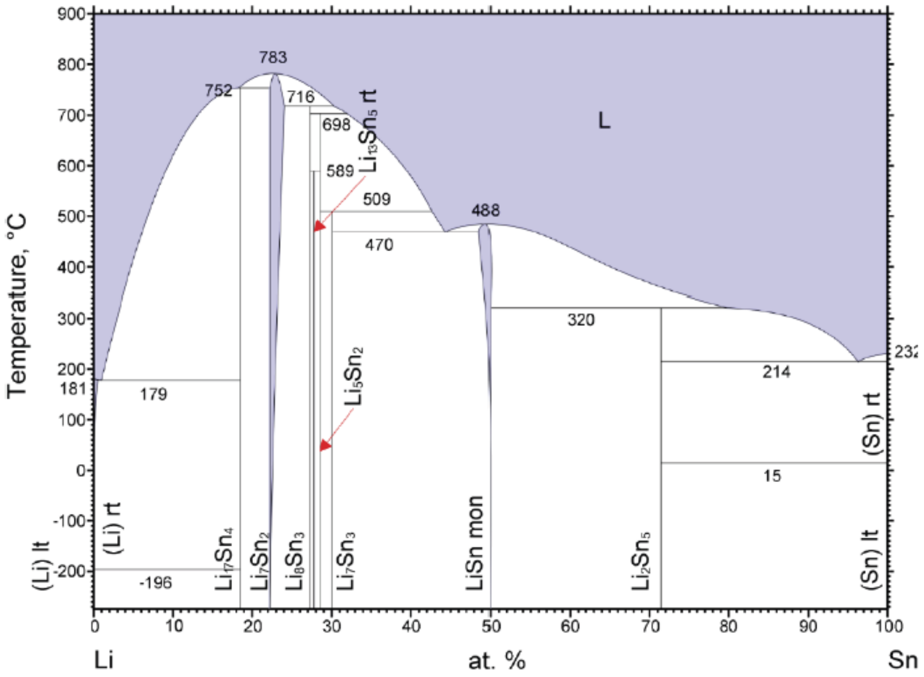


Fig. 7. LiSn phase diagram.

The other similar compositional batches for the DSC tests conducted resulted in the same trend as shown in Fig. 8 (with a magnified phase diagram region interested in). The pre-melted (sample #4) LiSn 73.3/26.7 had a sharp onset temperature of 719.5°C, whereas the LiSn phase diagram indicates that this composition has a melting temperature around 760°C.

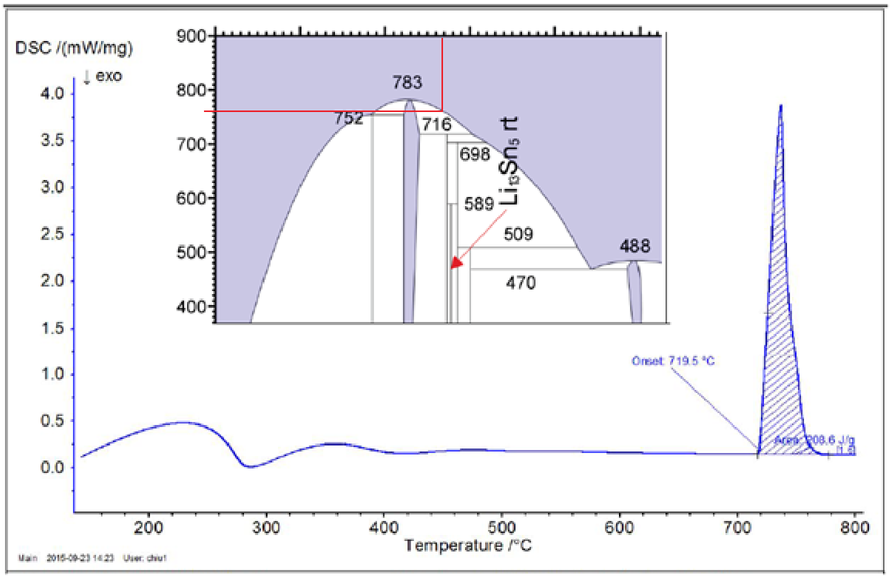


Fig. 8. DSC results for sample 4 and phase diagram in the region of interest.

In Fig. 9 we see that sample #2 (elemental mix of 60% Li, 40% Sn) shows a peak with the onset temperature at 529°C, while the Li-Sn phase diagram shows a melt temperature of 575°C.

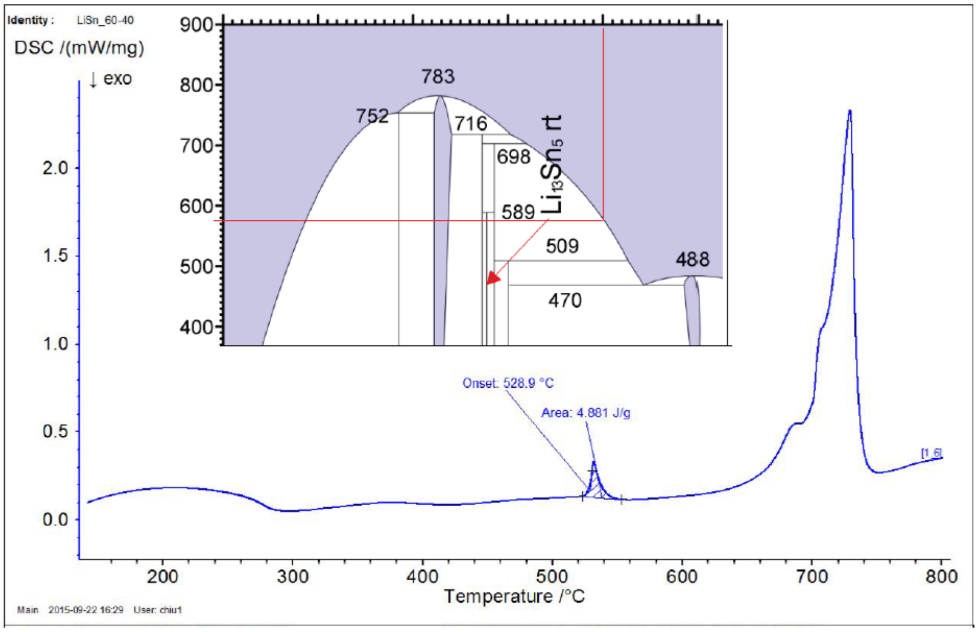


Fig. 9. DSC results and phase diagram for Sample #2.

Fig 10 shows the DSC results for Sample # 3 (pre-melted binary LiSn 93.3/6.7) along with relevance sectional phase diagram of LiSn system.

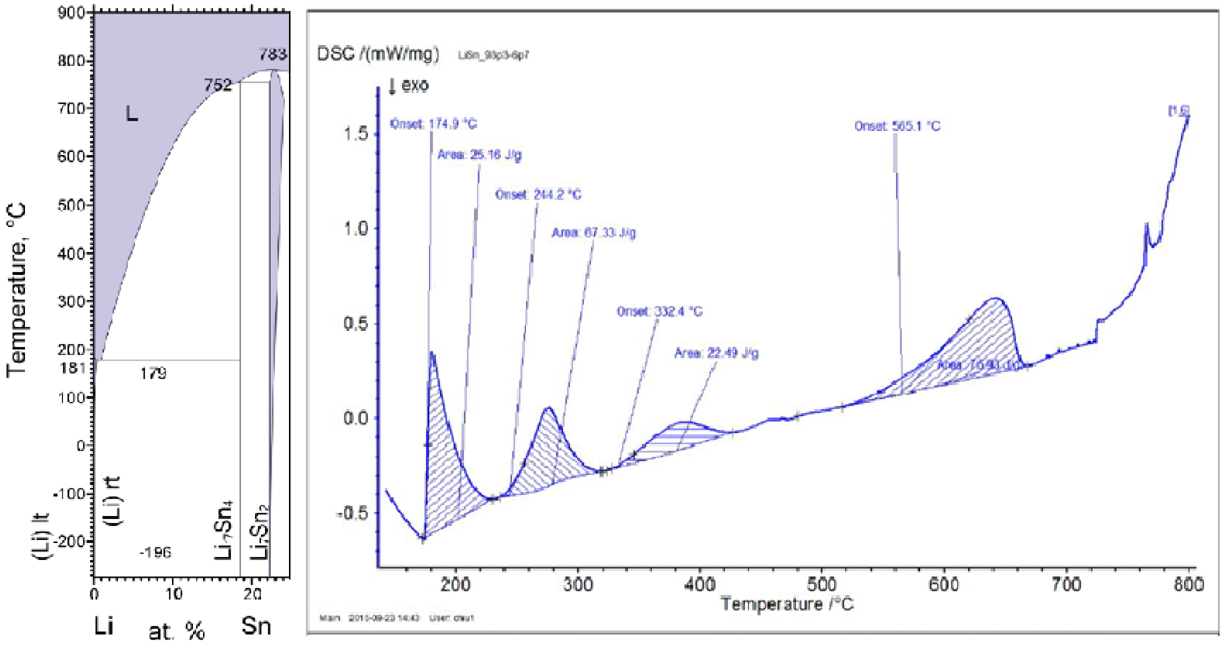


Fig. 10. DSC results and phase diagram for Sample #3.

As seen in DSC run, there exists a series of broad/sharp peaks that didn't match with the phase change/reaction in the proposed phase diagram. It is assumed that the raw material's contamination during sample handling/transferring between glove boxes etc., in the preparation process might have been happened. It is also likely there might have been some corrosive reaction with the pre-melting crucible/DSC holder at the high temperature. In some cases, a direct combination of lithium with nitrogen may quickly be forming lithium nitride (Li_3N). X-ray diffraction analysis has been used to examine such nature of black solid accumulated on Li metal surface when exposed in glove box atmosphere, whose result is shown in Fig. 9.

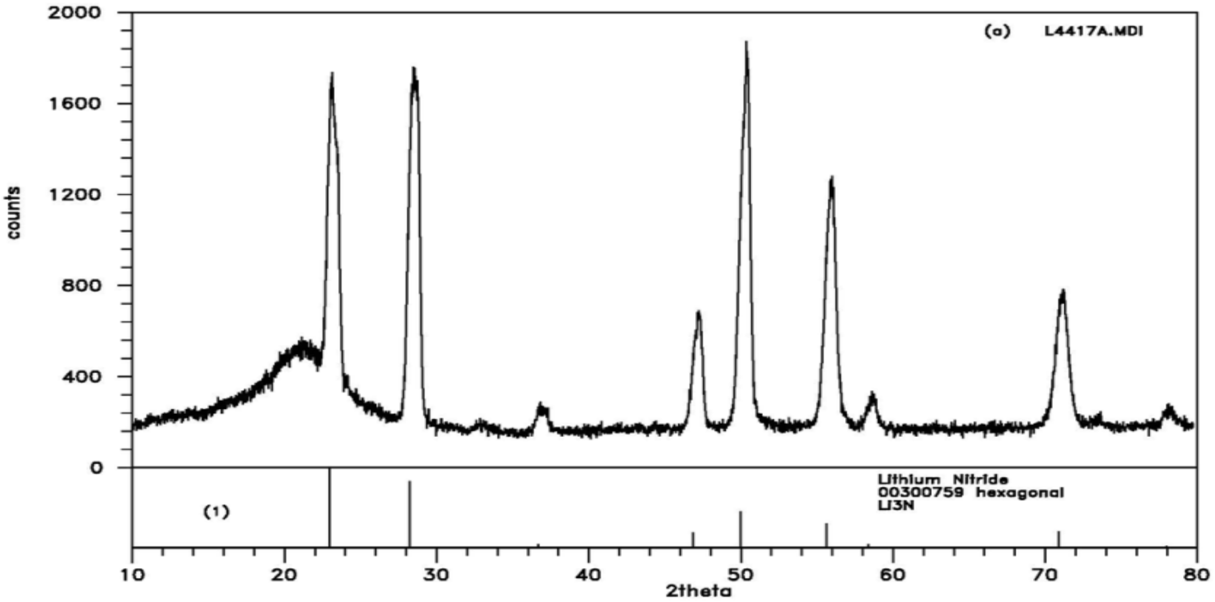


Fig 11. XRD analysis indicating the presence of Li_3N.

Likely there is a potential nitrogen contamination of lithium as being situated from inert GB. Note that $Li_3N + 3\ H_2O \rightarrow 3\ LiOH + NH_3$ reacts violently with water to produce ammonia.

5.2 Ternary Result and Comparison to Literature Melt Point

Using data for three binaries (LiSn, LiZn, and SnZn), Turchi conducted thermodynamic modeling to produce calculated isothermal sections of the ternary LiSnZn alloy system [2]. For example, of the predicted isothermal sections of the ternary LiSnZn alloy system at 700°C and 400°C are shown in Fig. 12. Unfortunately, we did not produce sufficient data during this LDRD to validate the predictions.

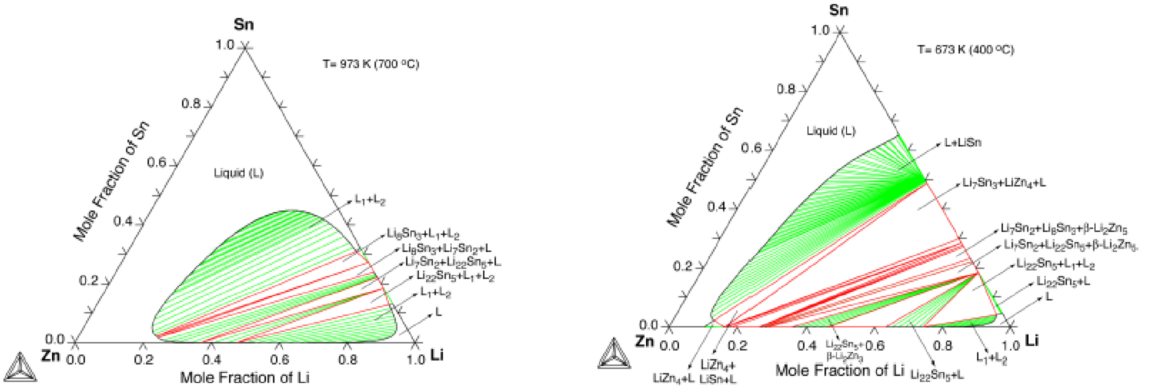


Fig. 12. Phase diagram prediction for LiSnZn alloys at 700°C (left) and 400°C (right) [2].

A result of the first ternary system for DSC run is shown in Fig. 13 for the sample #5 (ternary with elemental mix~ LiSnZn 60/20/20). It turned out to have a series of broad/sharp peaks. In a low temperature region of DSC curve, an onset at 291°C might have attributed to form a solid phase transformation into several compounds regions (such as Li_7Sn_2+Li_8Sn_3+β–Li_2Zn_5, and Li_7Sn_2+$Li_{22}Sn_3$+β–Li_2Zn_5, followed by a fractional melting at the onset of 500.05°C. However an onset of an endothermic reaction on DSC data at 736°C didn't match with any phase change/reaction in the proposed phase diagram indicating there could have been phases not captured in modeling.

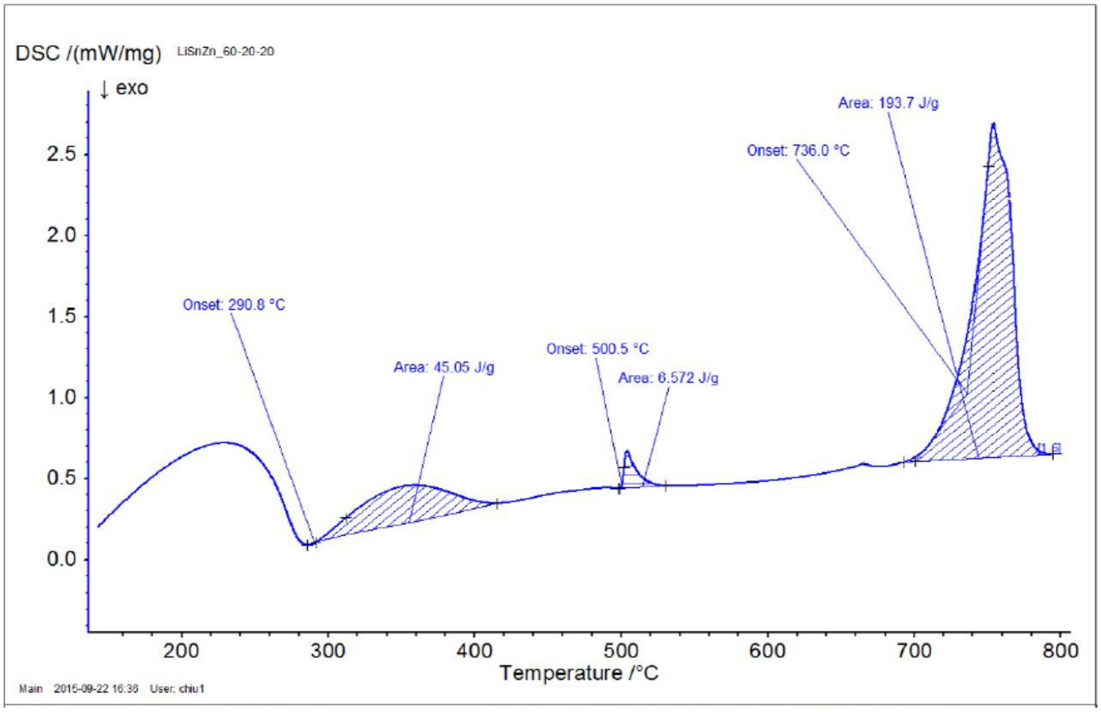


Fig. 13. DSC result for LiSnZn 60/20/20 ternary.

6. Sample Characterization Results

X-ray Diffraction (XRD) analysis has been utilized to identify the status of subjected materials, such as phases of powders prepared for DSC run: pre-melted ones and mechanically alloyed ones. The XRD sample was prepared by grinding with a laboratory pestle and mortar into fine powder form and loaded onto an air-sensitive holder. The XRD experiment was conducted on the Bruker X-ray diffractometer system utilizing Copper Kα radiation.

6.1 XRD for Binary sample (Mechanical Alloy part)

Figure 14 is a typical resultant XRD spectrum for a binary sample. This case shown here is for the mechanically alloyed powder of LiZn 80/20. Crystalline lines can be observed that do not match those of Li or Zn suggesting that an alloy of LiZn may have been produced as a single phase. The peak intensity does not match those from the data base for the LiZn system. Differences in peak intensity may possibly be due to different atomic compositions.

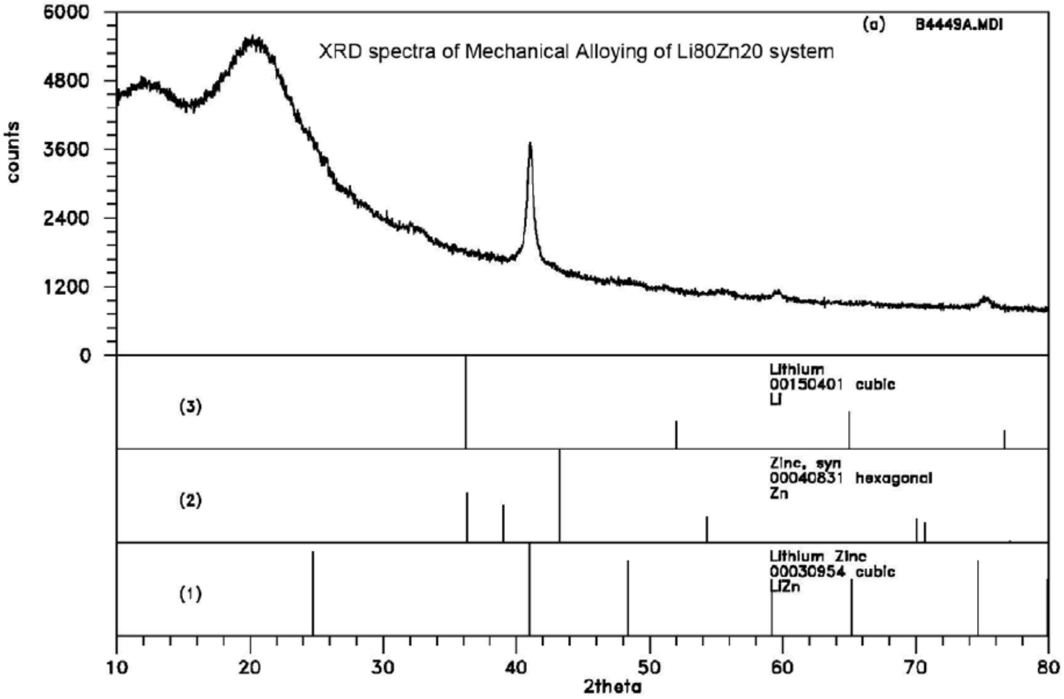


Fig. 14. XRD results for the LiZn 80/20 binary alloy.

6.3 XRD for Ternary Samples - (Melt Experiment part)

X-ray diffraction analysis has been used to examine the phase of the LiSnZn 60/20/20 which was brought into by pre-melted reaction (800°C for 4 hours). Figure 15 shows the resultant XRD spectra for this sample.

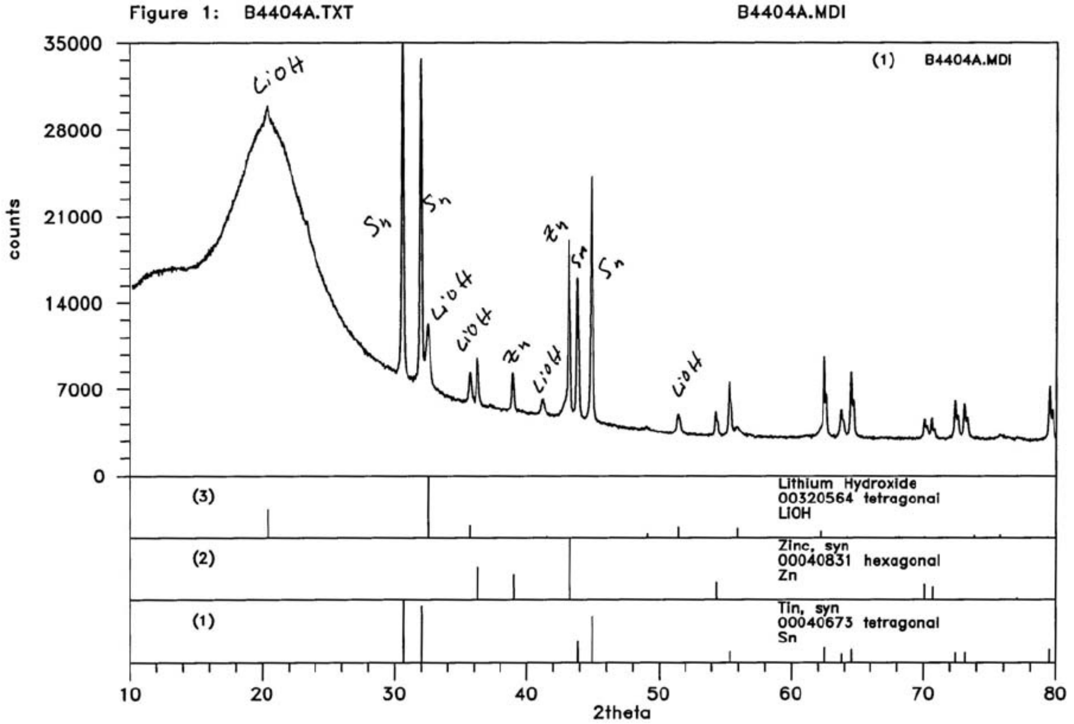


Fig. 15. XRD results for the LiSnZn 60/20/20 ternary alloy.

There are many crystalline lines observed in the XRD spectra which can be indexed to Zn, Sn and a probable minor phase of LiOH. The elements did not form any homogeneous compound phases even though the mixture was held at high temperature for a long time. It appears that the Li did not react with Sn or Zn. LiOH might have been formed due to poor glove box atmosphere control, with oxygen and hydrogen and/or generated during handling.

6.4 DSC Run Results (Mechanical Alloying)

Figures 16 and 17 show DSC results for the LiSnZn 60/20/20 and LiSnZn 70/20/10 ternary alloys, respectively. The results indicate the formation of single phase alloys with nice sharp onsets of phase change. This shows that the mechanical alloying process was effective.

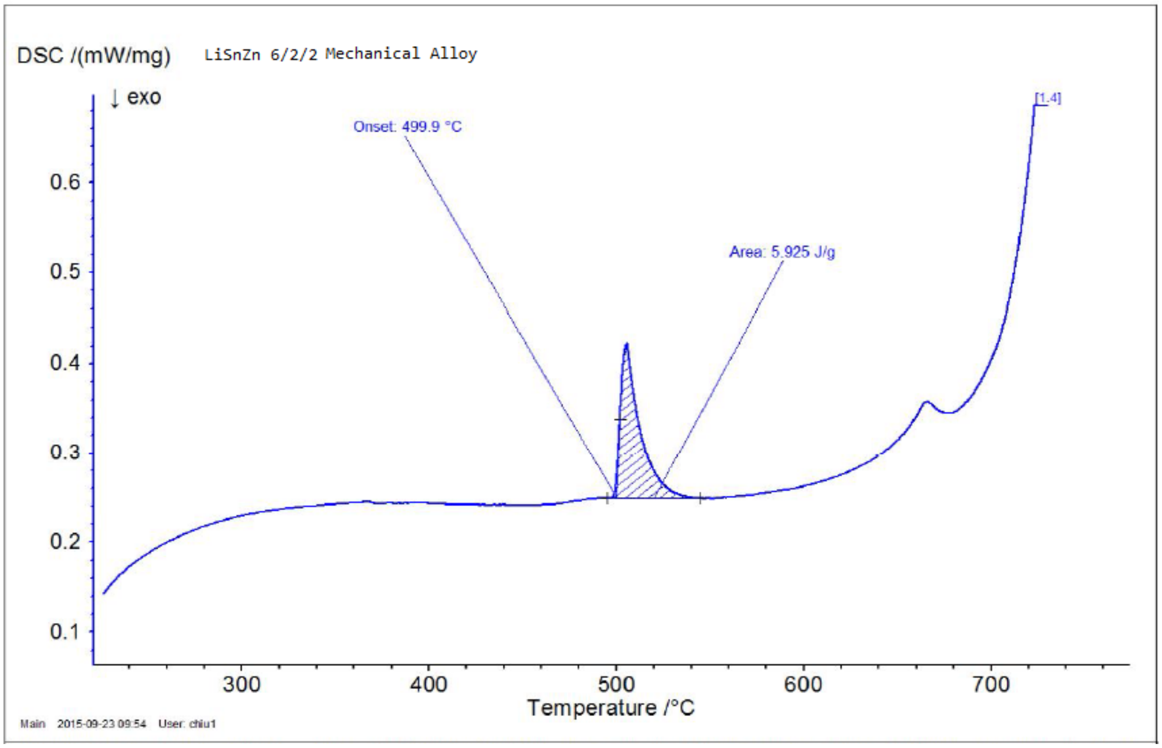


Fig. 16 XRD results for the LiSnZn 60/20/20 alloy.

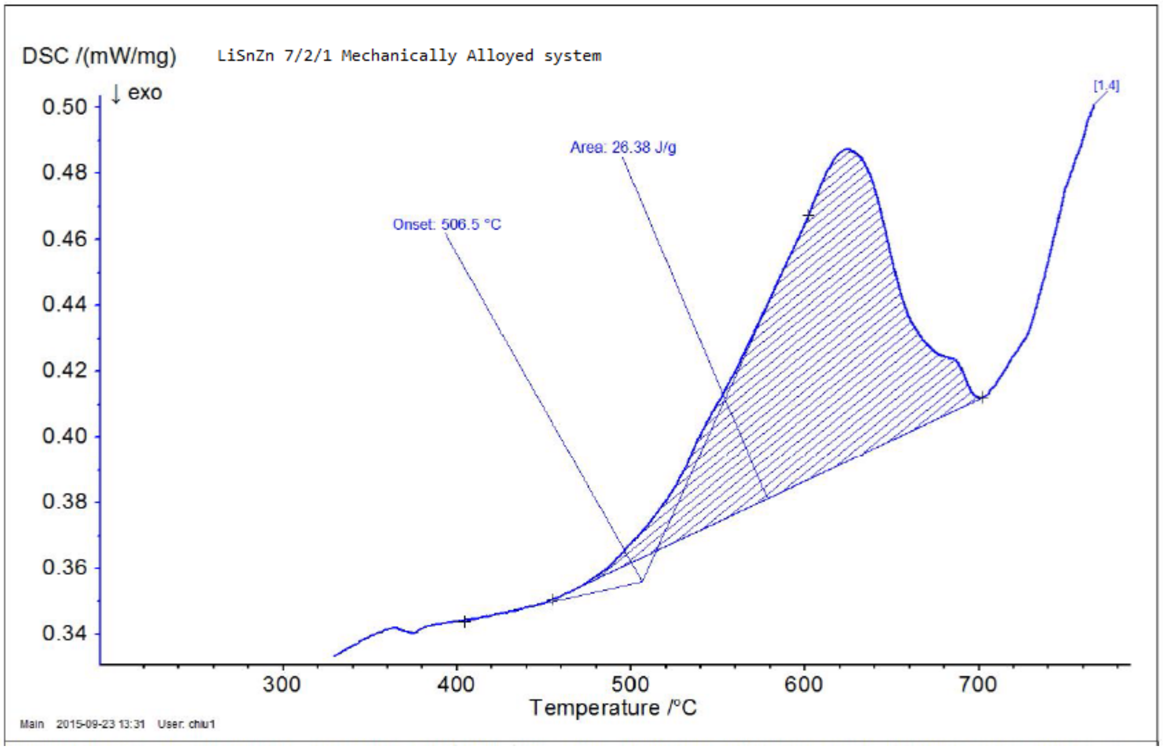


Fig. 17. XRD results for the LiSnZn 70/20/10 alloy.

7. Conclusions and Recommendations

The experimental part of the ternary alloy LDRD fell short of expectations due to a series of equipment and operational issues with the DSC as well as unexpected difficulties producing samples to be tested. By the end of the study, these issue were largely resolve, but at that point there was not time to get the data need to validate computationally predicted phase diagrams. Thus at this point we do not have a clear measure of the melt temperature of potentially viable ternary alloys for tritium breeding in a fusion blanket.

Some additional conclusions and recommendations are given here as an aid to future experimental work on this topic.

- The 60/20/20 formula had the sharp peak; the 70/20/10 formula had a very board peak over a very wide range in temperature. Based on the result, the 60/20/20 formula should be investigated further.
- A DSC analysis of the 60/20/20 formula with a temperature up to 650°C, instead of 800°C, should be conducted to see if the crystallization showed in the third cooling cycle.
- The DSC temperature rate of 10°C/min or 15°C/min should be considered to see if it shows better resolution.
- Sample preparation information and ID methodologies should be clearly established and be available for the DSC.
- An investigation is necessary to determine whether or not the tungsten crucible is the best suit for material used in the analysis.
- The DSC should have a spare sample carrier to prevent down time in case the existing one needs to refurbish.
- Several samples of each composition should be prepared to allow for multiple DSC runs which would give better statistics.
- XRD of post-run DSC samples should be conducted to be verify the phase again. Post-run compositional analysis via XPS and/or wet-chemical analysis should also be done.
- Base on trial and error for last couple of months of the study, mechanical alloying was found to be a viable technique to prepare single phase ternary alloy.

References

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