Identifying and Investigating Superconductivity in the RE_3MX_5 Compounds Ce_3TiBi_5, Ce_3NbSb_5, La_3TiBi_5, and La_3NbSb_5

Taryn Bailey

Abstract

Single-needled crystal structures of Ce_3TiBi_5, Ce_3NbSb_5, La_3TiBi_5, and La_3NbSb_5 were grown in a tin flux with the intent to understand the physical properties of these materials and identify them. In terms of this experiment, our focus is on synthesizing these crystals, isolating them, and identifying them through X-ray diffraction and Energy Dispersive X-Ray Spectroscopy (EDS) measurements. If we find an interesting compound has formed, then we can run further tests on its magnetic properties. La_3TiBi_5 had two different crystal shapes. The needle-shaped crystals exhibit some paramagnetic behavior and are comprised of tin and titanium (Sn_5Ti_6), according to EDS and X-Ray diffraction analysis. However, the cubic looking crystals in this batch contain La, Bi, and Sn according to EDS. The X-Ray data shows that the crystal is $LaSn_3$ of space group cPm-3m and superconducting at 5.25 K. The EDS measurements for Ce_3NbSb_5 and La_3NbSb_5 are very similar, leading to the conclusion that they are both NbSnSb; however, the XRD data does not agree. The crystals have flat four and five-sided faces that extend to a prism shape. The peaks of these crystals in the X-Ray data make it hard to identify these crystals as just NbSbSn, so further tests must be administered. EDS and X-Ray measurements confirm that Ce_3TiBi_5 crystals are just Sn crystals. Each crystal will need further testing to confirm its identity.

I. Introduction

Our investigation contributes to understanding the physical properties of superconducting materials. Superconductors are metals that carry electrical current efficiently because there is essentially no energy loss. Two main characteristics of superconductors are that they have zero electrical resistance and they expel their magnetic field when cooled below a critical temperature (T_c), thus transitioning to the superconducting state[1]. Superconductors can transport electricity at a much greater capacity than copper wire or other conducting materials used today. There are a limited amount of superconductors being introduced into the power grid; however, science surrounding how these materials operate is still minimal[1]. The disadvantage of superconductors is the fact that they traditionally must be kept at such low temperatures in order to super conduct that it is impractical to maintain these temperatures on a large scale in the real world[2]. Along with maintaining its magnetic properties, there are many conditions unknown to scientists under which materials are superconductive. Superconductors have great potential to influence how we use electricity in the future once science overcomes such limitations and reaches its goal of having superconductors function at room temperature.

At the University of Florida, the Hamlin Group utilizes high-pressure applications to understand the physical properties of known and unknown materials. The Hamlin Group has been experimenting with using such applications to manipulate materials so that they can enter a superconducting phase that isn't reachable at ambient pressures. More specifically, this project focuses on the growth and structural determination of unknown materials of the 3-1-5 compound ratio: Ce_3TiBi_5, Ce_3NbSb_5, La_3TiBi_5, and La_3NbSb_5. Previous investigations concentrating on the composition of such materials of the form RE_3MX_5 (where RE is a rare-earth metal, M is a main group or transition metal and X=Bi or Sb) reveal that there is a large class of these compounds, but few have been characterized by their magnetic properties or superconductive behavior. Here, I

report how we created these crystals and how we will identify them.

In previous work at the Hamlin lab, Ce_3TiSb_5 was synthesized and exhibited some interesting properties in its magnetization and resistivity, leading us to further investigate the RE_3MX_5 compounds. Structural unit cell determination can relate outer morphology to inner crystal structure. By knowing this information, we can apply magnetic fields along different axes and determine appropriate orientations to the crystal for examinations. The work surrounding Ce_3TiSb_5 tells us numerous features in magnetization and lends itself to interesting physics.

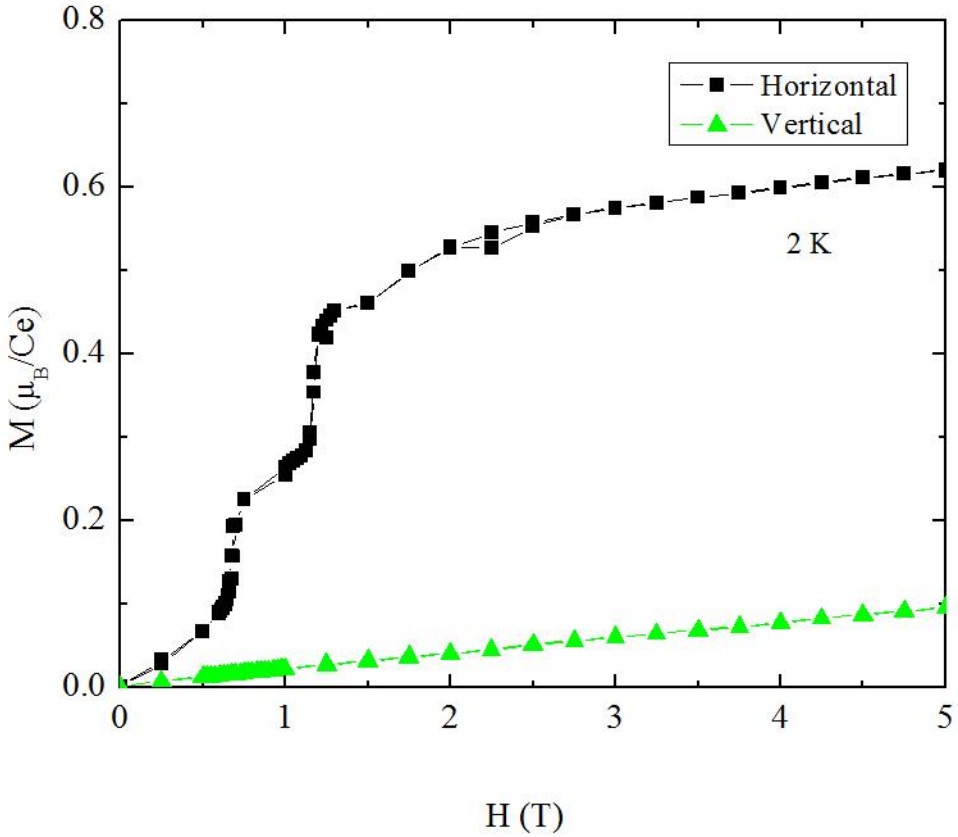

Figure 1. This is a plot of Magnetization v. Applied Field of both the vertical and horizontal alignment.

Figure 1 shows a meta-magnetic transition. The horizontal orientation has anti-ferromagnetism when the applied magnetic field is between 0 and 0.5 approximately. At the peak or maximum magnetism the sample becomes ferromagnetic. The interesting properties in this 3-1-5 compound make exploring other 3-1-5 compounds attractive. The following table is a pool of research from labs outside of the University of Florida that conveys what RE_3MX_5 compounds exist and have been studied.

Table 1: Possible 3-1-5 compound combinations[346789]

	5				
		Sb	Bi	Sn	Ge
1	Ti	La, Ce, Pr, Nd, Sm, U		U	U
	V	U			
	Cr	U			
	Mn	U	La, Nd, Ce		
	Sc	U			
	Zr	La, Ce, Pr, Nd, Sm, U			
	Hf	La, Ce, Pr, Nd, Sm, U			
	Nb	La, Ce, Pr, Nd, Sm, U			
	Ta	U			
	Mg		La		

The elements highlighted in purple are the rare-earth metals in RE_3MX_5.

The integration of rare-earth elements into the $RE3MX_5$ crystal structure is a rather new technique. Rare-earth elements are used as stabilizing agents that lower the dimensional features of the crystal's layers.[3] Similarly, ternary rare-earth antimonides may possess properties that are expected to be dimensionally unbalanced along different axes, but may also exhibit metallic or semi-metallic behavior[3]. Since ternary rare-earth antimonides possess structures where Sb atoms form isolated chains between and around the rare-earth atoms, electrical and magnetic properties could be affected based off of their structure.[4] Comparable to antimonides, the ternary rare-earth bismuthides (RE_3MBi_5) might also have an interesting structure that describes the magnetic and electrical properties of the compound; however, bismuthides research still remains underdeveloped[4]. Ce_3TiBi_5 and La_3TiBi_5 have not been previously synthesized, so by relating these compounds to the antimonides we hope to produce needle-like, hexagonal single crystal structures and test their magnetic properties for superconductivity.

II. Methods

A. Synthesis

All of the elements used for measuring are manufactured form Alfa Aesar. Starting materials for Ce_3TiBi_5 and Ce_3NbSb_5 consist of the rare-earth element cerium (99.8%); transition metals, titanium granules (99.9%) and powdered niobium (99.99%; Alfa Aesar Puratronic); metalloids, bismuth lump (99.999%; Alfa Aesar Puratronic) and antimony shot (99.999%). Starting materials for La_3TiBi_5, and La_3NbSb_5 contain the same transition metals, metalloids, and flux; however, we are using the rare-earth metal lanthanum rods (99.9%). We used a tin flux shot (99.99+%) for each sample.

Single crystal structures are intended to form under flux growth. The flux is the medium in which our chemical reaction will occur and what the single crystals will precipitate out of. For

purposes of this experiment, we used a theoretical value of 1.5g of tin flux where we used a 1 to 2 ratio of sample to flux. We measured each of the elements along with the tin flux in the 3-1-5 ratio masses using stoichiometric calculations and put them into a crucible. Due to scientific error, the mass of Ce in Ce_3TiBi_5 is 10 times less than the theoretical mass. The crucible was then loaded into an Argon filled Pyrex tube, which was then sealed inside a quartz tube and heated in a furnace. The flux will lower the melting point of the other elements in the crucible and re-form single crystals at the end of the furnace process. The firing schedule duration was four days. On day 1, the temperature ramped to 570°C to dwell for 10 hours. On day 2, the temperature ramped to 950°C in 4 hours and dwelled for 24 hours. On days 3 and 4 the temperature cooled to 700°C over 48 hours. Following this procedure, the crystals are well etched and ready for examination.

B. Isolating the crystals

Generally, the crystals maintain smooth, shiny surfaces with sharp edges and geometric shapes, while the flux has rough edges and is a dull misshapen clump. When the flux attached to a crystal we etched it off by putting it in an acidic solution that dissolved away the flux. The etching process was approximately a 1:1 ratio solution of HCl to H_2O. To avoid the HCl from attacking the crystal as well as the flux, we used a little less HCl in the solution after we repeated the etching process. We put the solution in the Sonicator for 20 minutes, rinsed with water and then put the crystals in water in the Sonicator for 10 minutes, then rinsed with ethanol. We repeated this process for each sample until we saw no more flux was attached to the crystals. Now by isolating these single crystal structures, we were able to take measurements to help further identify what the crystal is.

Ce3NbSb5

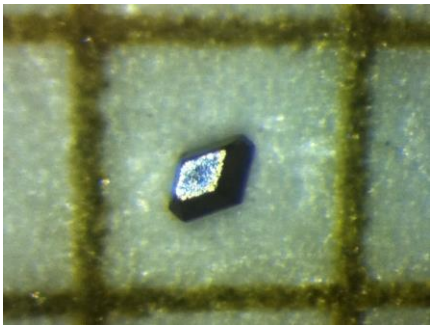

Figure 2. There were a couple of different crystal structures in this batch, but this was the primary shape. This crystal was placed on 1mm paper. The crystal is about 400 μm in length, 320 μm in width, and 200 μm in depth.

Ce3TiBi5

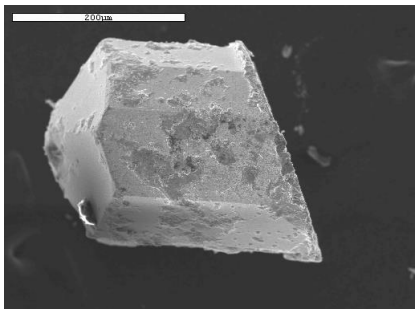

Figure 3. There were a couple of different crystal structures in this batch, but this was the primary shape. This is an image is generated by a SEM-scanning electron microscope. The dimensions are about 100 μm wide and 190 μm long.

La3TiBi5

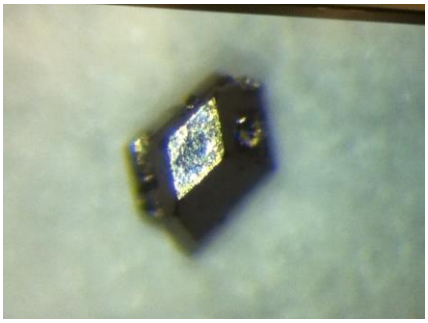

Figure 4. There were a couple of different crystal structures in this batch, but this was the primary shape. The crystal is about 500 μm in length, 400 μm in width, and 200 μm in depth.

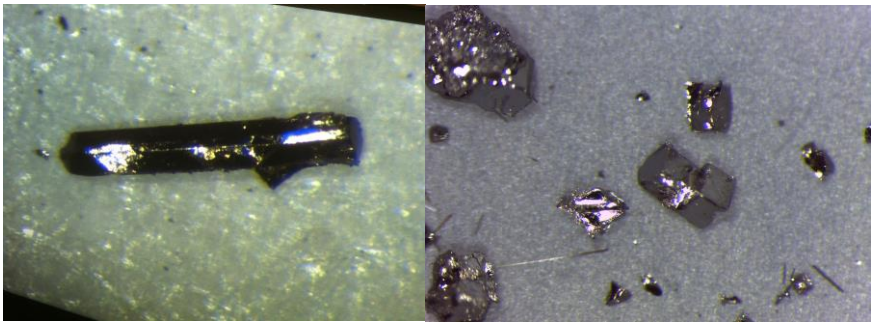

Figure 5. There are two types of crystal structures in this batch. On the left is an un-etched needle, hexagonal shape typical of the 3-1-5 structure. On the right, are un-etched cubic looking crystals.

The synthesis of these crystals resulted in these formations. Typically, the RE_3MX_5 structures are a hexagonal symmetric needle-shaped crystal. The only crystal that resembles this structure is one of the crystals that formed in the La_3TiBi_5 batch (Figure 5 on the left).

III. Results and Discussion

A. Structure Determinations

Single crystal and powdered X-Ray diffraction data were collected for La_3TiBi_5. Figure 6 displays an X-Ray diffraction pattern of the powdered cubic structures in this batch. The data

conveys that these crystals are best identified as $LaSn_3$ because the peaks best correspond to this compound. We calculated the lattice parameters for the La_3TiBi_5 unit cell by relating its composition to other 3-1-5 structures: a= 9.6832, b= 9.6832, c= 6.4671.

Figure 6: XRD for La_3TiBi_5

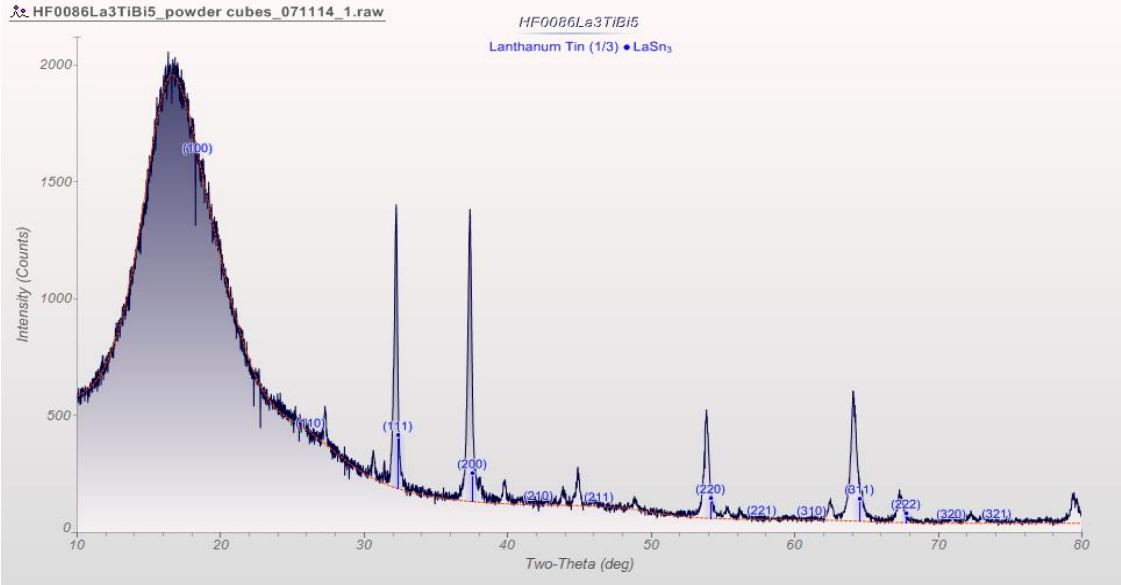

Figure 6. Diffraction pattern of Intensity v. 2θ for La_3TiBi_5 cubic crystals.

Table 2: EDS for La_3TiBi_5 for cubic crystals

Element	Atomic %	Compound ratio
C	62.35	--
O	18.66	--
Sn	7.97	7
La	1.11	1
Bi	9.92	10

The EDS measurement (Table 2) suggests that tin and bismuth are the primary elements within the crystal with some lanthanum. Carbon (C) was disregarded because the crystals were placed on carbon tape – not actually a part of the crystal composition. This statement is true for all other samples. The oxygen percentages are also disregarded. The microscope could pick up oxygen as a contamination factor rather than part the crystal composition. The X-Ray data suggests that the crystals are $LaSn_3$. A SQUID measurement shows that the cubic shaped crystals are $LaSn_3$.

Figure 7: SQUID measurement for La_3TiBi_5 for cubic crystals

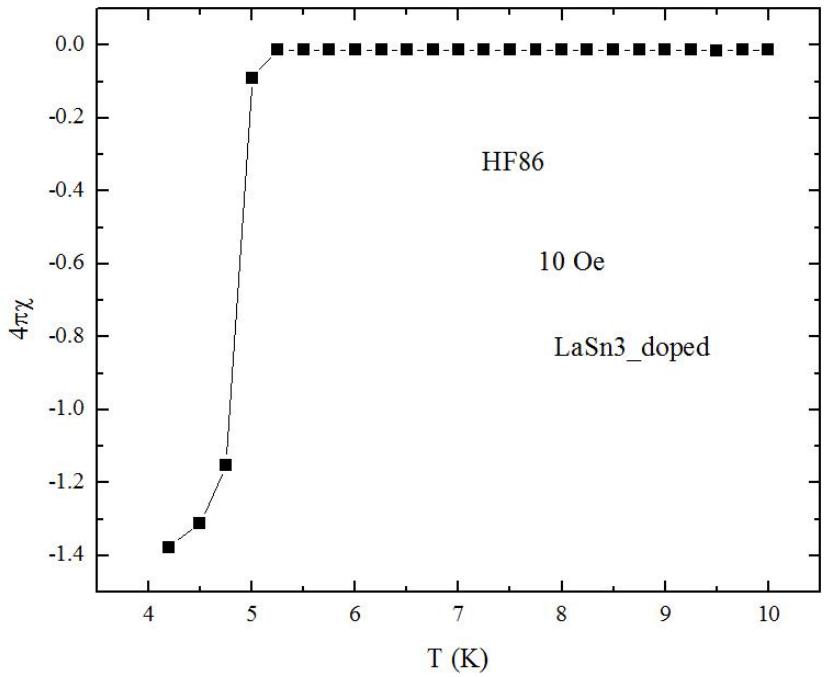

Figure 7. Plot of Magnetic Susceptibility v. Temperature in Kelvin. CGS units are used in these measurements.

According to Figure 7, it is the cubic structures that are superconducting rather than the typical needle-shaped crystals as expected. Studies outside of the Hamin lab report that $LaSn_3$ under pressure has a T_c = 6.5 K[5]; however, our data shows that the T_c = 5.25 K where the sample goes from zero magnetism and then transitions to being diamagnetic. The drop in the graph signifies the expulsion of the magnetic field. The T_c is reported lower than 6.5 K due to some doping from

bismuth. For perfect diamagnetism we would expect -1, demagnetization increased the field, $La_{(3-x)}Bi_x$**.** This data is in accordance with the X-Ray data; therefore, it is confirmed that the cubic crystals are superconducting and are identified as $LaSn_3$. We suspect that with further analysis using the PPMS measurements we can gather information on the crystal's resistivity.

Table 3: EDS for La_3TiBi_5 un-etched needle crystal

Element	Atomic %	Compound ratio
C	52.67	--
Ti	24.09	1
Sn	23.24	1

Table 3 indicates no lanthanum (La) or bismuth (Bi) was found. The Sn_5Ti_6 compound of space group hP63/mmc(194) peaks best correspond to the peaks produced by the crystal structure. We did an X-Ray on a single needle-shaped crystal to verify the EDS data.

Figure 8: XRD for powdered needle crystals of La_3TiBi_5

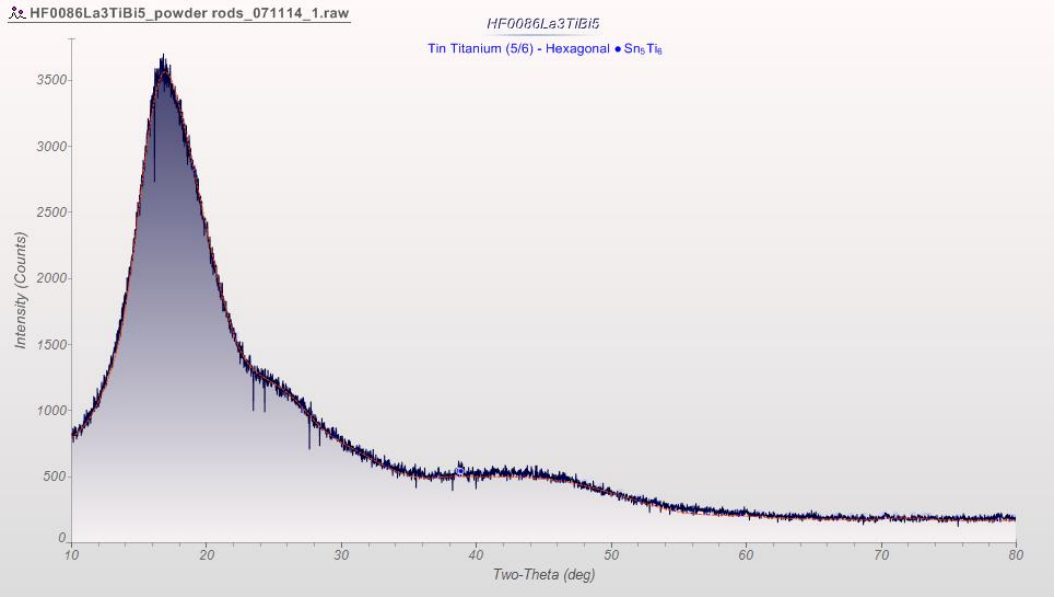

Figure 8. Diffraction pattern of Intensity v. 2θ for La_3TiBi_5 powdered needle crystals.

The data shows only one small peak where 2θ is approximately 39 degrees (Figure 8). Most of the Sn_5Ti_6 compounds have their highest peak at that same point; however, this is not enough data to discern what type of crystal this is. With the EDS and X-Ray measurements we suspect that these single-needle crystals are tin titanium; however, further tests should be administered to confirm this.

SQUID measurements were also done on the sample in order to understand magnetic behavior.

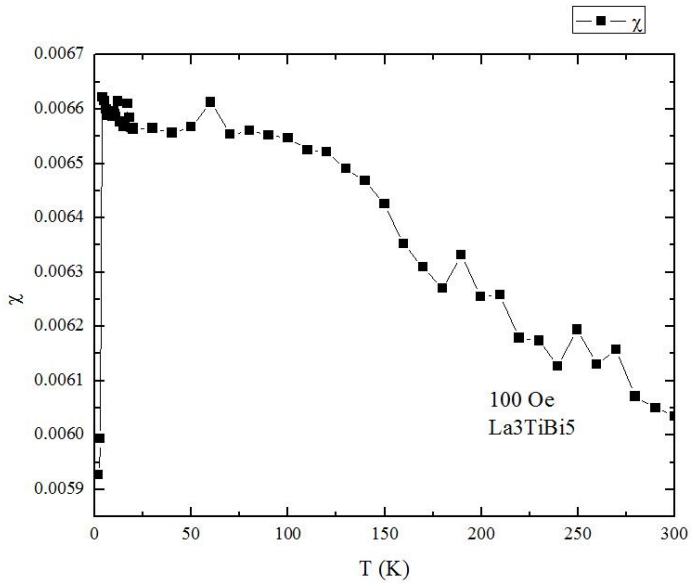

Figure 9. Graph Susceptibility v. Temperature for a La_3TiBi_5 single needle crystal (100Oe).

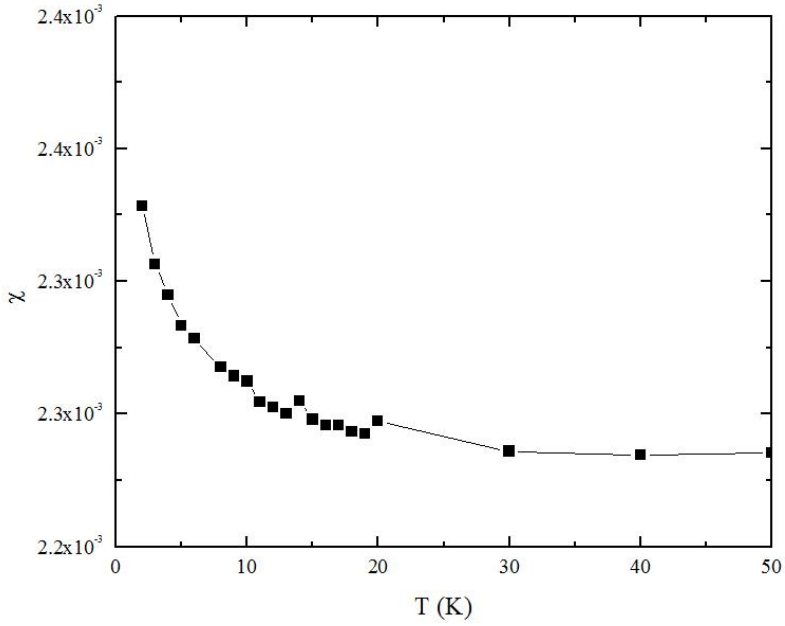

Figure 10. Graph Susceptibility v. Temperature for a La_3TiBi_5 single needle crystal with applied 1000Oe.

The steep drop in Figure 9 near 0 K is where the tin flux is superconducting and not the actual sample. Based on the results in Figure 10, the sample exhibits paramagnetic behavior.

Table 4: EDS for La_3TiBi_5 sanded needle crystal

Element	Atomic %	Ratio in compound
C	65.50	--
Si	1.17	--
Ti	16.84	1
Sn	16.49	1

This sample may have oxidized on the puck and did not give a clean surface to examine. Also, the presence of silicon may have been an impurity or residue from the crystal being sanded. For future tests we will use different crystals and keep them under Argon for storage.

Some single crystals were obtained from Ce_3NbSb_5 and La_3NbSb_5. Both of these samples reacted similarly and have the same crystal structure.

Table 5: EDS for Ce_3NbSb_5

Element	Atomic %	Compound Ratio
O	23.43	--
Nb	25.13	1
Sn	30.30	1
Sb	21.38	1
Ce	-0.23*	0

Table 6: EDS for La_3NbSb_5

Element	Atomic %	Ratio in Compound
O	32.92	--
Nb	16.59	1
Sn	26.22	1
Sb	23.88	1
La	0.39*	0

When these samples were etched, there was a remaining powder that when X-Rayed was just Sb.

The EDS measurements for both crystals reveal that Sb, Sn, and Nb were the main elements found

in the crystal. The rare-earth metal did not seem to react in the furnace. This could be attributed to insufficient flux in the sample, which is why the Ce or La did not dissolve in the flux and never reacted. The X-Ray data for both growths also showed some similarities in the diffraction pattern.

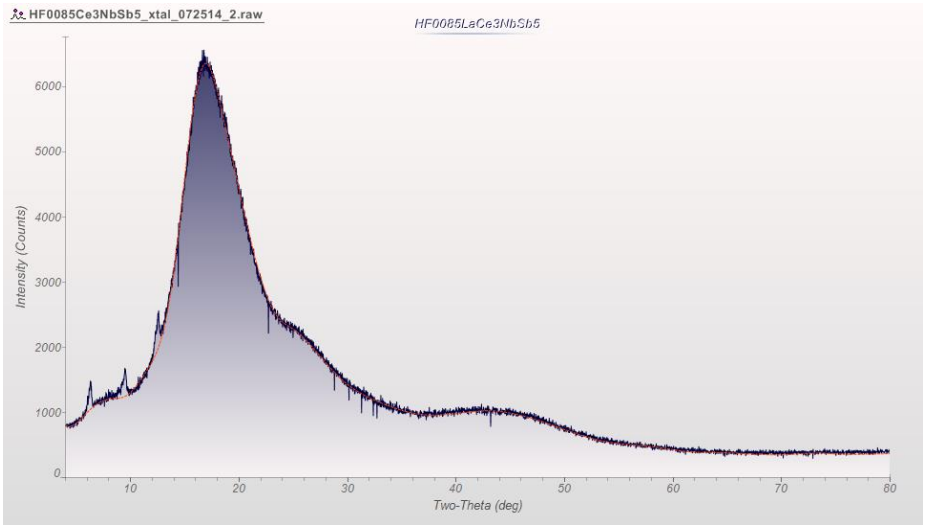

Figure 11. Graph of X-Ray diffraction plots Intensity in counts v. 2θ in degrees for Ce_3NbSb_5.

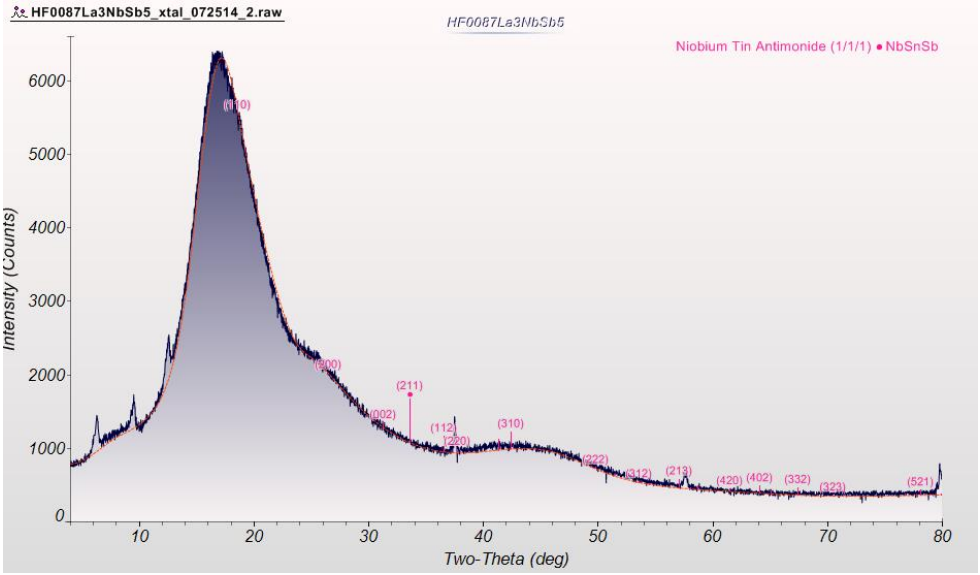

Figure 12. Graph of X-Ray diffraction plots Intensity in counts v. 2θ in degrees for La_3NbSb_5. NbSbSn compound does not match peaks.

Both X-Ray diffraction patterns (Figure 11 and 12) have three peaks between 0 and 15 degrees. Figure 12 has more peaks overall than Figure 11. This similarity along with the EDS measurements and the general shape of these crystals indicate that these crystals are of the same composition. Both crystals remain unidentified: it could be a new compound. SQUID and PPMS measurements are still pending.

The EDS and X-Ray measurements for Ce_3TiBi_5 reveal that the crystals formed in this batch are tin. However, based on the binary phase diagram, we took the samples out of the furnace at 700°C, which is much higher than the melting point of tin. The formation of tin crystals seems very unlikely.

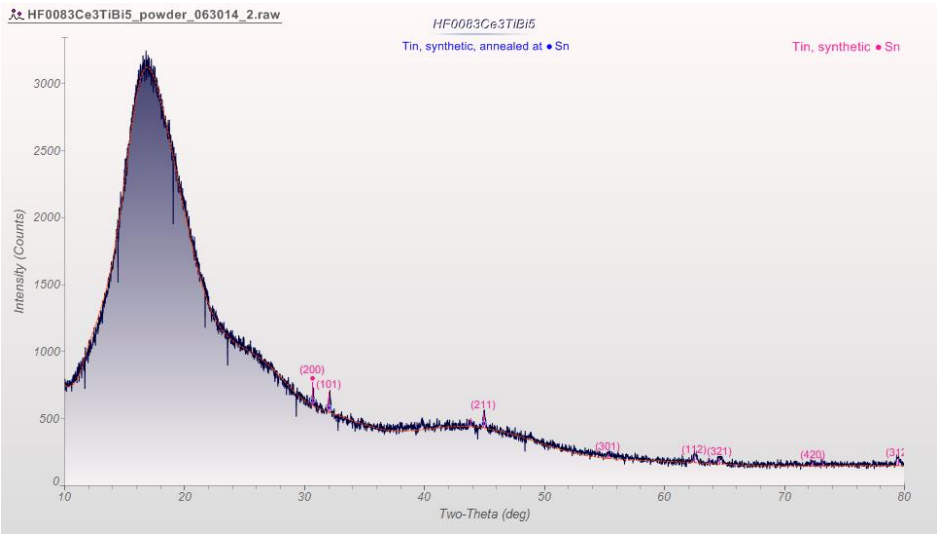

Figure 13. Graph of X-Ray diffraction plots Intensity in counts v. 2θ in degrees for Ce_3TiBi_5.

Table 7: EDS for Ce_3TiBi_5

Element	Atomic %	Ratio in Compound
C	77.70	--
O	1.37*	--

Sn	20.93	1

Tin crystals forming from this growth gives unexpected results. This could be attributed to an error in the synthesizing stage. We also suspect that the crystal was still covered with tin, which could explain the EDS data. This compound will undergo SQUID measurements and will be regrown as part of future work.

VI. Conclusion

There are still many unknowns about each of these samples. La_3TiBi_5 grew two different types of crystals. The single-needle crystals do not show magnetic properties that indicate superconductivity, but they could possibly be identified as Sn_5Ti_6. The cubic shaped crystals were superconducting and were identified as $LaSn_3$ doped by bismuth. Ce_3NbSb_5 and La_3NbSb_5 have the same shape and their XRD and EDS data show that these are the same crystal and the rare-earth metals did not react in the furnace. The Ce_3TiBi_5 is identified as a tin crystal, which doesn't seem accurate. The morphology looks like it should be Ce_3TiBi_5, but there were too few crystals to do more tests on it. None of the crystals produced we of the 3-1-5 composition. This could be attributed to the furnace scheduling or insufficient flux. All of these samples will be regrown and further tested as part of future work.

Acknowledgments

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