Preparing the components for testing superconductivity in ThFeAsN

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ABSTRACT

The iron pnictide superconductors have been a quickly expanding area of research in condensed matter physics. In 2016, a novel iron pnictide, ThFeAsN, was reported as a superconductor with a critical temperature of 30 K. For an oxygen free iron-based superconductor in the 1111-system, this critical temperature is much higher than has previously been seen. Here we prepare the compounds needed for the synthesis of ThFeAsN, and test the purity of these compounds with X-ray diffraction. This requires sintering pellets of iron and arsenic to create FeAs and nitriding thorium to create Th$_3$N$_4$. X-raying these compounds after synthesizing them revealed that we successfully avoided any such contaminants, as the diffraction patterns matched the Inorganic Crystal Structure Database data for both compounds. These can now be used for the synthesis of ThFeAsN. If superconductivity is confirmed in this iron-pnictide, without the oxygen contamination previously seen, this novel superconductor could be the key to further information on mechanisms of superconductivity and resulting material properties.
I. INTRODUCTION

High temperature iron-based superconductors, discovered in 2008, are a recent development in condensed matter research\(^1\). Each new family of superconductors opens up new opportunities for novel superconductivity mechanisms, material properties, and higher critical temperatures. With iron-containing compounds having previously thought to be unlikely candidates due to their magnetic properties, this new and vast area of superconductivity has been given much attention by researchers\(^1\). These superconductors have been found to have multiple properties ideal for being made into wire, which has further motivated research\(^1\). In addition, introducing other elements into the iron can boost the transition temperature; this effect is more significant than in cuprates, in which the additional elements can more easily compromise the superconductivity\(^2\). Therefore, with every new compound a multitude of tests needs to be done to fully explore its properties.

Recently, ThFeAsN was discovered as a superconductor of type-1111 (the ratio of each element) with a critical temperature 30 K without doping\(^3\). Aside from this, no iron based type-1111 superconductor without oxygen exists in the literature with a critical temperature above 10 K\(^1\). This suggests a potential for properties unique among other iron pnictides in the 1111 system. After initial experiments, the group that discovered this compound’s superconductivity also predicts that neither electron nor hole doping can increase the critical temperature of ThFeAsN\(^3\).

This project’s goal is to prepare the materials necessary (FeAs and Th\(_3\)N\(_4\)) to synthesize ThFeAsN, so that superconductivity can be confirmed and further tests, such as doping experiments, can be performed. Specifically, as the discoverers did, oxygen contamination must be carefully avoided, as the absence of oxygen is what makes this compound’s superconductivity
especially notable. The procedure used for the discovery\textsuperscript{3} of this compound’s superconductivity was closely followed. X-ray diffraction was used to check if the desired compounds were correctly synthesized. The diffraction patterns of the synthesized compounds matched those given in a database of crystal structures; therefore, ThFeAsN can now be synthesized with compounds that are known to be correct.

II. MATERIALS AND PROCEDURE

ThFeAsN was made with 7 9’s arsenic, 99.998\% iron powder (-22 mesh), high purity thorium, and ultra-high purity N\textsubscript{2}. The materials were always manipulated in an argon filled glove box kept at a consistent oxygen content of 1 – 5 ppm. The arsenic was ground and passed through a 270 mesh sieve. The resulting arsenic powder was mixed and again sieved through a 270 mesh screen with the iron powder in a 1:1 molar ratio. This mixture was pressed into quarter inch (0.635 cm) diameter pellets. The pellets were placed into an Al\textsubscript{2}O\textsubscript{3} (alumina) crucible, which was in turn placed in a niobium encasing that was sealed in an arc melter. Using a Lindberg furnace, this container was heated to sinter the FeAs pellets; it was ramped up to 500 °C at 75 °C an hour, kept at 500 °C for 10 hours, ramped up at the same rate to 900 °C where it was kept for 56 hours, and finally taken back down to room temperature at a cooling rate of 75 °C per hour. Sintering was performed free of oxygen due to the alumina crucible being sealed in the niobium encasement, and in addition a constant flow of argon was run through the furnace to further limit the oxygen content of the space near the sample. The reacted FeAs pellets were removed in the argon glove box and ground to 325 mesh, yielding FeAs powder ready for use in the synthesis of ThFeAsN. Thorium was filed into 270 mesh powder in the glove box, and placed inside an open alumina crucible. This was placed in the furnace and, with a ramp of 75 °C per hour, kept at 1000 °C for 130 hours while sitting in a steady flow of N\textsubscript{2}.
To determine the actual composition of the compounds above once they were synthesized, a Siemens D500 X-Ray diffractometer was used. Both compounds were smeared on an X-ray slide with petrolatum, and Th$_3$N$_4$, due to its air sensitive nature, was kept under a 100 micron thick covering foil. The data analysis software MDI Jade was used to fit the diffraction data of the synthesized compounds to the target compound’s diffraction pattern, as tabulated in the Inorganic Crystal Structure Database (ICSE). Any unexplained peaks in the pattern could then be compared against diffraction patterns of possible contaminants.

III. RESULTS

Given the mass of the initial thorium used in the synthesis of what was intended as Th$_3$N$_4$, it has been found that, assuming a contaminant free compound, the final product is approximately Th$_3$N$_{4.09}$.

In the FeAs data (Figure 1), there are very well defined peaks, and each one is in the same position as an FeAs peak in the database. In the Th$_3$N$_4$ data (Figure 2), the peaks are shorter and wider (and therefore represent a smaller difference from background than the FeAs peaks). Nevertheless, all but one of these peaks have a match in the database. The highest intensity and widest peak, at a two-theta of about 25 degrees, is not present in the Th$_3$N$_4$ ICSE data.
Figure 1 – The FeAs diffraction pattern. The curved peaks represent X-ray intensity spikes as measured for the synthesized compound. Each blue line marks a peak as given in the ICSE FeAs data. Each peak has a corresponding blue marker. The red residual along the top marks the difference at each point between the measured and database intensity values.

Figure 2 – The Th$_3$N$_4$ diffraction pattern. The curved peaks again mark measured intensity spikes, while the blue lines mark the placement of the spikes given in the database for this compound. Each peak has a corresponding marker, except for the tallest, widest peak, at a two-theta of 25 degrees.
IV. DISCUSSION

In the diffraction pattern measured for the compound synthesized to be FeAs, every peak is explained by a corresponding peak in the tabulated ICSE data for the compound. Therefore, with no unexplained spikes in the data, this compound is truly FeAs as intended. Almost every peak in the Th$_3$N$_4$ data is explained by the corresponding database entry, and so the other compound is mostly Th$_3$N$_4$ as intended. These peaks do not as sharply contrast with background as the FeAs data, but are still clearly present and match peaks found in the database for Th$_3$N$_4$. The largest measured Th$_3$N$_4$ diffraction peak is not accounted for within the compound’s pattern as given in the ICSE. This corresponds to the covering foil used to keep the air-sensitive compound isolated from the environment. An X-ray scan was run on just the foil for a previous project$^4$, and the diffraction data showed a peak with the same intensity at the same two theta.

The next step is to measure out the necessary FeAs, Th$_3$N$_4$, and additional thorium powder such that there is a 1:1:1:1 ratio between the four elements. The discovery of ThFeAsN was made after this mixture was put in a furnace in a quartz (SiO$_2$) ampule, but this leaves the danger of oxygen contamination, which was present in the superconducting compound after discovery$^3$. Instead, a beryllia (BeO) crucible manufactured by Brush Wellman will be used. The same X-ray diffraction method used to confirm the purity of the components of ThFeAsN will be used to confirm the final compound itself. If the synthesized material is free of contaminants and exhibits superconductivity (as shown by susceptibility measurements made by a superconducting quantum interference device, or SQUID) then ThFeAsN would truly be a novel superconductor without any doping required. Failure to superconduct would require more explorations, especially if the X-ray reveals contamination; further efforts to avoid such contamination would then be the goal.
V. CONCLUSION

The methods described here have produced pure samples of FeAs and Th$_3$N$_4$. The primary methods used, such as sintering and nitriding, are widely applicable to the production of varied superconductors that include these or similarly created compounds. Specifically, in the immediate future, these results now allow a confident synthesis of ThFeAsN.

The work done here then sets up what could prove to be the definitive test of the superconductivity of ThFeAsN. This compound has an electronic structure reminiscent of other iron-based superconductors, but is notable for its superconductivity and absence of magnetic ordering without any doping required$^5$. Therefore, proof of the superconductivity of this material could lead to a better understanding of the type of compound in which superconductivity can arise. Furthermore, other novel material properties may be awaiting discovery, as past efforts to contribute to the ever expanding catalogue of the iron-pnictides have proved illuminating.

ACKNOWLEDGMENTS

This work was made possible my Dr. Gregory Stewart, who provided much instruction and guidance. Dr. James Hamlin provided the needed X-ray measurements. Additional aid was given by Dr. Jung Soo Kim and Gordon Tam. This lab position was made available by the Research Experience for Undergraduates (REU) site at the University of Florida. This program was funded by the National Science Foundation grant DMR-1461019.
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