Optimization of a non-arsenic iron-based superconductor for wire fabrication

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Abstract
We report on the optimization of synthesis of iron selenide-based superconducting powders and the fabrication of selenide-based wire. The powders were synthesized by an ammonothermal method, whereby Ba is intercalated between FeSe layers to produce Ba$_{x}$(NH$_3$)$_{y}$Fe$_2$Se$_2$, with tetragonal structure similar to AFe$_2$X$_2$ (X: As, Se), ‘122’, superconductors. The optimal $T_c$ (up to 38 K) and Meissner and shielding superconducting fractions are obtained from the shortest reaction time ($t$) of reactants in liquid ammonia (30 min). With the increase of $t$, a second crystalline 122 phase, with a smaller unit cell, emerges. A small amount of NH$_3$ is released from the structure above $\sim$200 °C, which results in loss of superconductivity. However, in the confined space of niobium/Monel tubing, results indicate there is enough pressure for some of NH$_3$ to remain in the crystal lattice, and thermal annealing can be performed at temperatures of up to 780 °C, increasing wire density and yielded a reasonable $T_c \approx 16$ K. Here, we report of the first successful wire fabrication of non-arsenic high-$T_c$ iron-based superconductor. Although bulk materials are estimated to carry critical current densities $>100$ kA cm$^{-2}$ (4 K, self-field), the current transport within wires need to be optimized ($J_c \sim 1$ kA m$^{-2}$).

Keywords: iron based superconductor, selenide wire, non arsenic

(Some figures may appear in colour only in the online journal)

Introduction

A family of iron-based superconductors adopts crystal structures of I4/mmm ThCr$_2$Si$_2$-type tetragonal framework, with ‘122’ chemical formula (figure 1). This family is based on AFe$_2$X$_2$ (A = alkali or alkaline-earth metals; X = Se, As) [1–4]. The structures are composed of edge-shared FeX$_4$ tetrahedral layers separated by A [4]. The iron selenium (non-arsenide) materials (FS), have the second largest superconductivity critical temperature ($T_c = 30$–45 K) [1–8] after the rare-earth (R) ‘1111’ family of RFeAsO ($T_c = 56$ K). The 122 family is considered as a good candidate for high-field applications because of its high critical field, $H_{c2}$ [9], irreversibility fields ($H_{irr}$) [10], and $J_c$ values [11, 12], in combination with its weak field-dependence on $J_c$ [13, 14]. It is also more adaptable for technological use because it can be made without critical R elements [4], has sharper resistive transitions [15] and lower electronic anisotropy ($\gamma_H \approx 1$–2) than other iron-based superconductors [16, 17]. Moreover, 122 offers intrinsic pinning associated with atomic-scale defects resulting from chemical doping [15, 17] and has a large $J_c$ up to 500 kA cm$^{-2}$ (2 K) [11, 14]. In addition, the behavior of $J_c(H)$ can be approximately constant with $J_c(8$ T) remaining high at $\sim$100 kA cm$^{-2}$ [18]. In addition, 122 can be completely free of toxic arsenic (As) in AFe$_2$Se$_2$ (FS) [1–4], which is the material of focus of this manuscript.

The FS that are prepared by high-temperature synthesis techniques (e.g. Bridgman) [19–21] are typically referred to as ‘245’ (instead of 122) due to their iron-vacancy disordered structure (e.g. in $A_{x}$Fe$_{2-x}$Se$_2$) [22]; their superconducting...
properties are sparse with evidence of non-pure products and phase separations [22–27]. For FS that are synthesized by a low-temperature ammonothermal route, higher purity products are evident with bulk superconducting behavior [28, 29]. Although this solution method allows for greater ease of intercalation of larger alkaline-earth metals and rare earths (for A) between FeSe layers [28, 29], non-deliberate intercalation of ammonia is likely within the spacer layer, producing a Fe-vacancy-free phase of A\textsubscript{x}(NH\textsubscript{3})\textsubscript{y}Fe\textsubscript{2}Se\textsubscript{2} (we call ‘N122’) [30]. For N122, the superconducting properties may be controlled by electronic doping and lattice expansion, which in turn modify both $T_c$ and the amount of superconducting shielding fraction [30]. Although the in-plane lattice parameters of 245 and N122 are comparable within a narrow range (3.78–3.96 Å), the c-lattice parameter for N122 is expanded compared to 245, which offers evidence of co-intercalation of larger spacer molecules (such as NH\textsubscript{3}) together with A. For example, the structure of K\textsubscript{2}Fe\textsubscript{2}Se\textsubscript{2} produced by the high-temperature method is reported with I4/mmm and $c \approx 14.04$ Å [1] while that synthesized from ammonothermal reaction was indexed using two larger unit cells (LCs) with $c \approx 16.16$ and 20.48 Å [29]; the latter inhomogeneous product may be due to the diffusion-controlled intercalation process. Evidence for N122 co-intercalation by ammonia is additionally offered by neutron diffraction experiments for A = Li [30], and is also seen in the resulting smaller c-lattice parameter through de-intercalation by heating to $\sim$200 °C [31].

In an effort to understand and optimize superconductivity in FS, here we focus on A = Ba in AFe\textsubscript{2}Se\textsubscript{2} because it has negligible air-sensitivity (compared to alkali metals such as K), has the highest reported $T_c$ value among FS, and promises reliable bulk superconductivity [29]. We have systematically explored the impact of variations in ammonothermal synthesis conditions on the structure and properties, and in particular on the possible role that intercalated NH\textsubscript{3} molecules play in the development of superconductivity for Ba\textsubscript{x}(NH\textsubscript{3})\textsubscript{y}Fe\textsubscript{2}Se\textsubscript{2}. Due to its lower toxicity compared with arsenic iron-based superconductors (e.g. Ba\textsubscript{1-x}K\textsubscript{x}Fe\textsubscript{2}As\textsubscript{2}) and higher $T_c$ compared with 11 selenides (i.e. FeTe\textsubscript{1-x}Se\textsubscript{x} crystals with max $T_c=15$ K) we make some conclusions about this material’s potential for wire applications by drawing wire while maintaining a critical current.

**Experimental**

For the synthesis of N122 BaFe\textsubscript{2}Se\textsubscript{2}, first the tetragonal $\beta$-FeSe had to be synthesized from iron granules (Alfa Aesar, 99.98%) and selenium shots (Alfa Aesar, 99.999+%) that were sealed in double-walled evacuated fused silica ampoules. The ampoules were heated to 700 °C and held for three days, then the temperature was raised to 1065 °C over three days to form a melt, followed by annealing at 420 °C for three days, after which the product was quenched in an ice-bath. Grinding the slate-gray powder increased the proportion of unwanted hexagonal $\delta$-FeSe or Fe\textsubscript{7}Se\textsubscript{8}, which was subsequently substantially reduced by annealing the powder in vacuum at 420 °C for several more days. Intercalation of small pieces of dendritic barium (Alfa Aesar, 99.9%) into $\beta$-FeSe powder proceeded by loading stochiometric amounts of each material in a 100 mL Schlenk tube, in the ratio of Ba:FeSe = 0.5:2 (or in some samples 0.55:2), in a helium-filled glove box with <1 ppm of O\textsubscript{2} and H\textsubscript{2}O. Using a vacuum-gas manifold, approximately 20–25 mL of Na-dried liquid ammonia was condensed onto the reactants at liquid-nitrogen temperatures. The NH\textsubscript{3} was then allowed to gradually warm to room temperature in the sealed Schlenk vessel, with magnetic stirring begun once the ammonia had liquefied. (Warning: vapor pressures in the range of 8–10 bar are obtained near room temperature over liquid ammonia.) The reaction was complete once the deep blue color of the ‘solvated electron’ had disappeared. The products were kept in liquid NH\textsubscript{3} for a total of $t \approx$ 30 min (S30m), 5 h (S5h), or 3 days (S3d); please note that these notations will be used to denote these samples for the rest of this manuscript. After these reaction times, the excess ammonia was condensed into a second Schlenk vessel to isolate the product. The resulting black powder was collected and stored in a helium-filled glove box, with care taken to avoid possible reaction in air. Although the products of Ba\textsubscript{x}(NH\textsubscript{3})\textsubscript{y}Fe\textsubscript{2}Se\textsubscript{2} are not air-sensitive in the short term, a gradual decline in crystallographic quality was observed in air over several days.

Powder x-ray diffraction was performed using a PANalytical X’Pert PRO MPD employing a Ni-filtered Cu–K\textsubscript{α} radiation source. The data were analyzed by Rietveld refinement using GSAS-EXPGUI [32, 33]. Ba\textsubscript{x}(NH\textsubscript{3})\textsubscript{y}Fe\textsubscript{2}Se\textsubscript{2} was indexed to the ThCr\textsubscript{2}Si\textsubscript{2}-type crystal structure with I4/mmm space group. The barium content, x, was refined using 0.5 as the starting point, while attempts to include NH\textsubscript{3} in the structure provided minimal improvement in agreement indices, and was finally excluded. Dc magnetization measurements proceeded using a Quantum Design Magnetic Properties Measurement System. Zero-field cooled (ZFC) and field-cooled (FC) magnetization measurements were performed at 10 Oe from 5 to 50 K, since the magnetization varied linearly with applied field below 100 Oe at 1.8 K noting full shielded response for a superconductor, magnetic susceptibility is presented as $\chi = -1/(4\pi)$. ZFC magnetization
data were also collected at 1 kOe from 5 to 300 K (not shown), and did not follow a Curie–Weiss law behavior. $M$ versus $H$ magnetization loops at 4 K were measured upon increasing field to 6.8 T, decreasing to ~6.8 T, then up to 6.8 T, for the estimations of $J_c$. Mass loss measurements were performed using a Perkin Elmer Pyris 1 thermogravimetric analysis (TGA) instrument located inside a helium-filled glove box with <1 ppm O$_2$ and H$_2$O; ~20 mg of Ba$_4$(NH$_3$)$_5$Fe$_2$Se$_2$ powder was loaded into a ceramic pan with heating at a rate of 40 °C min$^{-1}$ from 40 to 800 °C under a 20 L min$^{-1}$ flow of He. A portion of the evolved gasses was directed through a fused silica capillary into a Hewlett-Packard 5970 quadruple mass selective detector (MS); molecular masses were scanned at a rate of 1.63 scans/s from 5 to 500 AMU. A significant atmospheric N$_2$ baseline arises from contaminated Ba surfaces, or may be the result from the reaction of residual, loose, Ba with air-moisture during x-ray diffraction data collection. Table 1 summarizes the results, while figure 3(b) shows the trend in the size of lattice parameters $c/a$ with decreasing temperature; no change in the linear trends was observed around $T_c$.

The temperature dependence of normalized magnetic susceptibility, $4\pi\chi(T)$, on S30m, S5h, and S3d are shown in figures 4(a), (c), and (e), respectively. The $T_c$ values are in the range of 35–38 K (taken as the divergence of ZFC and FC), with higher $T_c$ noted for shorter reaction times. Similarly, the shielding and Meissner fractions decrease with increasing $t$. For example, the superconducting fraction drops from 76% for S30m to ~20% for S3d, and the Meissner fraction declines from 14 to ~3%, respectively. The $\chi(T)$ measurements were done on multiple samples from each of the batches, and were found to be reproducible. Additionally, S3d demonstrates a positive offset of FC data, suggesting the development of paramagnetic domains through the prolonged contact with liquid NH$_3$. Field dependence of magnetization, $M(H)$, is shown in figures 4(b), (d), and (f) for two quadrants only. No upper critical field is observed up to 6.8 T. In order to estimate the critical current density at 4 K, we used Bean’s formula; $J_c = 30\Delta M/(R)$, where $\Delta M$ is the difference in magnetization at 6 T, and $(R)$ is the average particle size estimated from scanning electron micrographs (SEM) of the powders, which are typically ~10 μm. The $J_c$ values on polycrystalline powders (not wires) are estimated in table 1.

The TGA–MS results for the different reacted materials (S30m, S5h, and S3d) are shown in figure 5. Mass loss for Ba$_4$(NH$_3$)$_5$Fe$_2$Se$_2$ proceeded in either two or three steps. All plots show $T_{onset,max} \approx 370$ °C and $T_{onset,max} \approx 280$ °C, while S30m and S3d also show a small $T_{onset,min} \approx 150$–200 °C, which is not separately distinguished in the S5h plot. Nonetheless, the combined mass loss at $T_{onset,min}$ and $T_{onset,med}$ is similar for all three samples ($\Delta m_{280°C} \approx 0.6–0.9%$ total mass), corresponding to ~0.12–0.19 NH$_3$ molecules per formula unit, assuming a composition of Ba$_4$Fe$_2$Se$_2$ for the remaining elements. The mass loss related to $T_{onset,max}$ shows much greater variation, ranging from $\Delta m_{370°C} \approx 2.4%$ for S3d to $\Delta m_{370°C} \approx 3.6%$ for S30m, corresponding to a loss of 0.50–0.75 NH$_3$ molecules per ‘Ba$_4$Fe$_2$Se$_2’$, respectively. These values can be combined to derive $y = 0.66$ for S3d to $y = 0.87$ for S30m. As previously noted, the mass spectrographs include a large N$_2$ background signal due to an atmospheric back-leak from the MS exhaust pump; however, the peaks corresponding to mass loss in the TGA were derived entirely from NH$_3$.

Several annealing studies were performed using sample S5h. Ba$_4$(NH$_3$)$_5$Fe$_2$Se$_2$ powder was pressed into pellets and sealed in fused silica tubes under various atmospheres (vacuum, 0.3–0.9 atm NH$_3$ gas, 0.3 atm Ar gas). These were

Results

The powder x-ray diffraction patterns for the products S30m, S5h, and S3d are shown in figure 3(a). In each case, two phases adopting the ThCr$_2$Si$_2$-type tetragonal structures were observed, differing primarily in the length of the $c$-lattice parameter. The LC generally had a $c$-parameter of ~16.7 Å, while the smaller unit cell (SC) adopted a $c$-axis length near 15.6 Å (table 1). The relative proportion of SC increased with increasing $t$, i.e. S30m gave LC:SC $\approx 76:10$ by mass, while S3d showed LC:SC $\approx 10:77$. Table 1 shows that the Ba–Se bond length in both tetragonal phases is longer than would be expected for direct bonding to occur ($\approx 3.4$ Å) [34]; this may suggest that NH$_3$ co-intercalates along with barium to push the FeSe layers further apart, or at least that the interactions are weak. In addition to 122 tetragonal LC and SC phases, several impurity phases were observed, including Fe$_2$Se$_8$ and both orthorhombic and monoclinic phases of Ba(OH)$_2$·H$_2$O. Although efforts were made to use shiny, un tarnished silvery Ba pieces, the presence of barium hydroxides may have originated from contaminated Ba surfaces, or may be the result from the reaction of residual, loose, Ba with air-moisture during x-ray diffraction data collection. Table 1 summarizes the results, while figure 3(b) shows the trend in the size of lattice parameters $c/a$ with decreasing temperature; no change in the linear trends was observed around $T_c$. 
then heated to between 150 and 200 °C for 24 h. The results for the sample post-annealed in Ar at 200 °C shown in figure 6 are typical of what was observed under all annealing conditions. Structurally, the LC phase disappears completely, leaving only the SC phase and an increased proportion of $\beta$-FeSe (figure 6(a)). The magnetic susceptibility (figure 6(b)) shows the complete suppression of superconductivity. The origin of the broad maximum at $\sim$100 K is not fully

**Figure 2.** The optical cross-sectional images of Ba$_x$(NH$_3$)$_y$Fe$_2$Se$_2$ wires of: (a) as-drawn; (b) post-annealed at 780 °C for 3 days; and (c) rolled, then annealed at 780 °C for 3 days.

**Figure 3.** (a) X-ray powder diffraction patterns for samples with different reaction time in liquid NH$_3$ (S30m, S5h, S3d); tick marks at the bottom indicate the diffraction peaks for known phases, from top to bottom: LC N122, SC N122, orthorhombic Ba(OH)$_2$·H$_2$O, monoclinic Ba(OH)$_2$·H$_2$O, and Fe$_x$Se$_y$. (b) Comparison of lattice parameters, $a$, $c$, and $c/a$ at room temperature and below 45 K, showing the trend in shrinking lattice upon cooling, as expected.

**Table 1.** Structural data, $T_c$, and $J_e$ estimates for Ba$_x$(NH$_3$)$_y$Fe$_2$Se$_2$ powders. Ammonia molecules were omitted from the refinement, i.e. only the Ba$_x$Fe$_2$Se$_2$ 122 lattice was considered. For the refined structural parameters, the LC phase is shown on the top line, with the SC phase on the bottom.
understood, but likely derives from paramagnetic impurities that exhibit short range or lower dimensional correlations.

Figure 7 shows the temperature dependence of normalized electrical resistivity for Ba$_x$(NH$_3$)$_y$Fe$_2$Se$_2$ wires. In general, the $R(T)$ is similar in these two materials, having $T_c \approx 16$ K.

In order to achieve a superconducting transition in the wires, thermal annealing of the wires was necessary at 780 °C, as described above, with worse superconducting results at other annealing temperatures. At such high temperatures, it is possible for some of NH$_3$ to leave the crystal lattice that cause structural and $T_c$ degradation, compared with
bulk material. A two-step transition observed below $T_c$ could result from a small but noticeable spatial distribution of $T_c$ within the crystals, being slightly smaller for the annealed (as-drawn, non-rolled) sample. Since Nb metal has a much lower $T_c$ and does not have a continuous conducting path due to its reaction with $\text{Ba}_x(\text{NH}_3)_y\text{Fe}_2\text{Se}_2$, it does not contribute to the superconducting properties of $\text{Ba}_x(\text{NH}_3)_y\text{Fe}_2\text{Se}_2$ wires. The presence of better superconducting characteristics in this sample are also highlighted by the critical field value. As shown in the inset of figure 7(a) the critical field of the rolled sample is estimated to be 13 T. For the annealed wire the value of $H_c2$ is higher and an analysis using the Werthammer–Helfand–Hohenberg model [35, 36] leads to $H_c2 \sim 21$ T. Figure 7(b) shows the temperature-dependence of critical current density of the superconducting wires. The overall shape of $J_c$ is typical of superconducting wire that is just discovered. The inset of figure 7(b) presents a magnetic-field dependence of $J_c$ at 4 K. Such transport data demonstrates the proof-of-concept for non-arsenic based wires with $I_c$.

Discussion

Based on x-ray diffraction patterns, the LC $\text{Ba}(\text{NH}_3)\text{Fe}_2\text{Se}_2$ phase initially forms in the ammonothermal reaction of Ba with $\beta$-FeSe, gradually decomposing with increasing reaction time to form the SC phase (figure 3). Based on TGA–MS data (figure 5), the decrease in LC phase appears to result from a loss of structural NH$_3$, which also correlates with a decrease in superconducting fraction for the powders (figure 4). These data combine to suggest the existence of LC phase as the primary superconducting phase. This conclusion is supported by annealing studies of powders (figure 6), where the complete suppression of superconducting behavior is accompanied by the disappearance of the LC phase in favor of the SC phase. It is likely that the structural variation that increases the unit cell length in the LC phase also plays a role in inducing superconductivity. This result is contrary to the situation discovered for the analogous K$_x(\text{NH}_3)_y\text{Fe}_2\text{Se}_2$ system as described by Ying et al [31] where the phase with the LC was found to have a lower $T_c$ than the smaller cell phase. The TGA–MS results (figure 5) seem to indicate at least two distinct mechanisms of NH$_3$ intercalation. One possible explanation is that NH$_3$ intercalates at two different sites, with the majority entering ‘stable’ sites and a smaller amount entering less stable sites or on the surface, which release ammonia at lower temperatures. The annealing studies may suggest that occupation of these lower stability NH$_3$ sites leads to the LC and induction of superconducting behavior. If this were the case, one would expect a larger amount of ammonia to be released at the first step in samples with larger superconducting fractions, i.e. S30m. This is contrary to what is observed, in that S30m actually has the smallest mass loss at lower temperatures of the three samples presented. A more likely explanation is that NH$_3$ occupies only one site, but undergoes partial decomposes to NH$_2^-$, resulting in more than one onset temperature as the amine further decomposes to N$_2$ and H$_2$. In this scenario, the SC powder phase only requires a certain minimum amount of NH$_3$/NH$_2^-$ to remain stable, while any ‘excess’ ammonia expands the unit cell and induces superconductivity. This explanation requires better structural understanding of $\text{Ba}_x(\text{NH}_3)_y\text{Fe}_2\text{Se}_2$ than can be
determined from traditional powder x-ray diffraction techniques. Neutron studies of Li$_x$(NH$_3$)$_y$Fe$_2$Se$_2$ have determined only one NH$_3$ site with disorder in the position of the hydrogen atoms [28], while synchrotron x-ray diffraction has indicated a similar arrangement for the Ba-system [37]. Furthermore, it remains unclear whether ammonia is the only intercalated species, or whether amine (NH$_2^-$) also enters the structure, and whether the chemical distinction between them has any bearing on superconducting properties, a possibility raised by Scheidt et al [30].

This is the first report of successful wire fabrication of (non-arsenic) high-$T_c$ 122 iron-based superconductor, with Ba(NH$_3$)$_2$Fe$_2$Se$_2$ composition. Further optimization is necessary to improve the transport $J_c$ and $T_c$ within wires. Although high $J_c$ values are found in bulk materials ($>100$ kA cm$^{-2}$), wires only carry $J_c$ $\sim$ 1 kA cm$^{-2}$. Overall, this manuscript demonstrates the proof-of-concept for non-arsenic based materials and wires that can have $I_c$. There will be room for improvement, as for the arsenic wires and over the years, there have been increases in $J_c$. For example, for Co–Ba$_{122}$ PIT wires, $J_c$ is increased to $\sim$ 8–9 kA cm$^{-2}$ by high-pressure processes of hot isostatic pressing or texturing using uniaxial pressure [38]. The $J_c$ of Ba$_{1-x}$K$_x$Fe$_2$As$_2$/Ag tapes is enhanced to $\sim$100 kA cm$^{-2}$ at 6 T by the combination of process of cold flat rolling and uniaxial pressing [39]. Textured PIT tapes of Sr$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ give weak field-dependence at 4.2 K, with 17 kA cm$^{-2}$ at 10 T, and 14 kA cm$^{-2}$ at 14 T [40]. Moreover, seven-core Ag/Fe sheathed PIT wires of Sr$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ achieved $J_c$ $\sim$ 20 kA cm$^{-2}$ at 4 K and self-field [41]; this study was followed by those on tapes with Sn additions giving $\sim$100 kA cm$^{-2}$ at 10 T and 4 K [42]. For Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ proton irradiation has given critical current densities that exceed 5 MA cm$^{-2}$ at 7 T and 5 K, along $c$ [43]. With such literatures on arsenic 122 s, it seems likely to improve $J_c$ values non-arsenic 122 s as well.
Conclusion

This is the proof-of-concept for the first successful wire fabrication of (non-arsenic) selenium-based iron-based superconductor. For powders of $\text{Ba}_x(\text{NH}_3)_y\text{Fe}_2\text{Se}_2$, ammonia in stabilizing superconductivity in $\text{Fe}_2\text{Se}_2$. However, in the confined space of niobium/Monel tubing, thermal annealing at 780 °C maintains superconductivity. We have successfully demonstrated the preparation of superconducting wires of selenide-based materials with $H_{c2}$ ~ 21 T and carrying current critical. To the best of our knowledge, this is the first report, and the proof-of-concept for the first successful wire fabrication of (non-arsenic) selenium-based iron-based superconductor.

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