Stoichiometry of tetragonal and hexagonal Fe$_x$Se: phase relations

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Abstract

Precise compositional analyses at spatial resolution $<1$ $\mu$m, combined with structure determination using bulk (i.e. powder XRD) and individual grain (i.e. EBSD) techniques, show that both $\beta$-Fe$_x$Se and $\delta$-Fe$_x$Se form as solids in a two-phase field above and below the apparent peritectic temperature of 457 $^\circ$C. Microstructures show that $\beta$-Fe$_x$Se and $\delta$-Fe$_x$Se form together via exsolution when cooled from this two-phase field; evident when annealing time and temperature are optimised. Using a facile one-pot method with elemental Fe:Se reactant ratios ranging from 0.95 to 1.14, $\beta$-Fe$_x$Se occurs as the predominant phase in association with hexagonal $\delta$-Fe$_x$Se in the temperature range 330 $^\circ$C $< T_{\text{max}} < 750$ $^\circ$C, where $T_{\text{max}}$ is the sintering temperature. Maximum yield of $\beta$-Fe$_x$Se occurs after sintering at $T_{\text{max}} > 690$ $^\circ$C with annealing at 420 $^\circ$C for $\sim$24 h. We define a modified phase diagram that includes this two phase field with $\beta$-Fe$_x$Se and $\delta$-Fe$_x$Se for 1.02 $< x < 0.90$ and a second two phase field with $\beta$-Fe$_x$Se and $\alpha$-Fe for 1.08 $< x < 1.02$. This revised phase diagram for Fe:Se $\sim$ 1.0 suggests that the peritectic transition nominally identified at $x = 1.04$ is not evident.

Supplementary material for this article is available online

Keywords: iron chalcogenides, stoichiometry, phase diagram, microstructure, superconductivity

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

1. Introduction

Transition metal chalcogenides have received significant interest in recent years due to their extensive range of applications in thermoelectrics, solar cells, sensors, magnetic devices, batteries, photocatalysts, semiconductors and superconductors [1]. The discovery of superconductivity in iron based compounds [2, 3] has led to intense scrutiny of chalcogenides including of the basic structural units that make up new families of superconductors through judicious substitution of other elements [4]. Superconducting iron-based compounds are classified into two groups: iron pnictides and iron chalcogenides [3, 5].

Iron chalcogenides have an advantage of lower toxicity and simpler crystal structure compared with iron pnictides [6, 7]. However, preparing single phase superconducting material is challenging. Iron selenides are found in several stable crystalline forms: tetragonal $\beta$-Fe$_x$Se, hexagonal $\delta$-Fe$_x$Se, orthorhombic FeSe$_2$, hexagonal FeSe$_2$ and monoclinic Fe$_3$Se$_4$ [8, 9]. Among these phases, the tetragonal $\beta$-Fe$_x$Se with PbO structure (space group P4/mmm) transitions to a superconductor (SC) with orthorhombic space group Cmma at $\sim$8 K [2].

To date, reports on the synthesis of tetragonal $\beta$-Fe$_x$Se powders describe a range of heat treatment protocols including reacting and annealing at several different temperatures followed by cooling or quenching to room temperature. For example, experiments by McQueen et al [10] show that product with a high proportion of $\beta$-Fe$_x$Se (i.e. $> 95\%$) can
be achieved with extended reaction and annealing times. This work employed long reaction times (>3 d) at high temperatures (>1000 °C), re-grinding the products and extensive annealing times (~2 d) at lower temperatures (300 °C to 400 °C), to obtain an optimum composition of β-Fe1₀₀Se for which the superconducting transition temperature, Tc, is 8.7 K [10].

In contrast, Grivel [11] demonstrates that short reaction times (e.g. between 1 and 10 h) at temperatures of 400 °C and 700 °C, influence the proportion of other phases formed in addition to β-Fe₅₆Se, the predominant phase. Long reaction times up to 100 h reduces the XRD-detectable proportion of other phases such as α-Fe and δ-Fe₄₅Se [11]. In a related study, Guo et al [12] show that the quenching temperature (between 300 °C and 500 °C) results in minimal change in the lattice parameters of β-Fe₅₆Se and has limited effect on Tc, (Δ~ 0.3 K).

Studies on β-Fe₅₆Se synthesis and phase relations [2, 10, 12–14], utilise refinements of bulk high resolution neutron diffraction data to estimate stoichiometry of the synthesized products. In one case, these diffraction data are supported by bulk ICP-OES analyses of the synthesized phases [12]. However, there are few, if any, studies that correlate structure (i.e. bulk x-ray diffraction and individual grain electron diffraction), microstructure and separately determined chemical analyses of individual grains from the same syntheses.

In this study, we present correlated phase, microstructural and crystallographic data on β-Fe₅₆Se synthesized using methods characterised as ‘low temperature’ [11]. We present data that, contrary to existing phase diagrams, shows a two-phase region above and below ~457 °C. Furthermore, we confirm that β-Fe₅₆Se transforms to the superconducting orthorhombic structure in the presence of δ-Fe₅₆Se for 1.02 < x < 0.90 with minimal effect on Tc, value [11, 12].

2. Materials and methods

Data presented in this study are a summary of more than 40 separate experiments across a range of temperatures, heat profiles and precursor starting material ratios.

2.1. Iron selenide syntheses

All preparations and pre-processing of materials are undertaken within a controlled atmosphere glove box containing 99.99% purity Argon with < 5 ppm O₂. Molar ratios of iron powder (99.9% purity, particle size ~10 µm) supplied by Alfa Aesar and selenium powder (99.9% purity; particle size ~149 µm) supplied by Sigma-Aldrich are weighed, ground in an agate mortar and pressed into a pellet of ~1 g. The pellet is placed into a boron nitride crucible housed within the reactor and filled with Ar. Further details of the reactor configuration and methods of use are provided in earlier publications [15, 16]. The tightly sealed reactor is removed from the glove box, placed onto the heating element and filled with Ar gas to pressures ranging between 0.56 MPa to 1 MPa at room temperature (~25 °C).

Table 1 summarises key parameters for reactions and the products of reaction presented in this work. A consistent heating rate of 1.66 °C min⁻¹ (100 °C hr⁻¹) is used for many reactions and at different reaction temperatures the heating rate is held constant for various time periods. A heating rate of 0.33 °C min⁻¹ (20 °C hr⁻¹) is used for Runs 11–15. For all syntheses, the reactor is cooled to room temperature by radiant loss consistent with the observation by others [13, 14] that quenching from these temperatures is unnecessary. We estimate the reactor cools to room temperature within two hours. Reaction 9 in table 1 is an exception for which the reactor is slowly cooled to room temperature over 45 h. All products are placed in the glove box for transfer from the reactor for further characterisation.

2.2. Characterisation

Polycrystalline samples are characterised by x-ray powder diffraction using Co Kα1 radiation in a Bragg-Brentano geometry with 0.02 2θ steps and a counting time of 10 s per step using a PANalytical x-ray diffractometer. Diffraction patterns are refined and indexed using the software program Topas; quantitative estimates of phase abundance in each product are determined by Rietveld refinements using Topas. In general, phase abundances determined by this technique are within <5% relative error [18]. X-ray diffraction patterns indicate that many synthesised products contain multiple phases with tetragonal Fe₅₆Se, hexagonal Fe₅₆Se, Fe₅₆Se₂, Fe₅₆Se₃ and FeSe₂ in variable proportions depending on the synthesis conditions listed in table 1.

For selected syntheses with high proportions of β-Fe₅₆Se phase, precise refinements of structural parameters were undertaken using a corundum internal standard and longer x-ray collection times. These refinements systematically varied cell parameters and Se occupancy to obtain the best fit to x-ray diffraction data for β-Fe₅₆Se. Se occupancy was refined as it is a general position in the tetragonal P4/nmm space group.

Microstructural and compositional analyses are performed on polished samples mounted with conductive resin and placed in a 30 mm diameter mould inside a mounting press. In general, final powder products contain 20 µm to 60 µm aggregates and are prone to ‘plucking’, or loss of whole grains, when polished. This attribute results in variable finish to the polish on individual grains.

During analysis, each grain was examined for suitability of surface finish to minimise inaccurate data collection. Sample mounts are polished with a series of diamond pads and cloths to a mirror finish suited to electron probe microanalysis (EPMA) and electron back-scattered diffraction (EBSD). EBSD data are obtained on selected samples using a field emission JEOL 7001 SEM with automated feature detection and equipped with an Oxford Instruments SDD XMax 50 mm² detector, EBSD pattern analyser and Channel 5 analysis software. EBSD mapping is performed with an accelerating voltage of 15 kV and a step size of 0.5 µm.

Quantitative elemental analyses are obtained using a JEOL JXA 8530F field emission EPMA equipped with five
Table 1. Selected starting conditions and products\textsuperscript{+} for FeSe syntheses.

| Run No | Starting rate Fe:Se (C min\textsuperscript{-1}) | Heating rate T\textsubscript{max} (C) | t\textsubscript{hold} (h) | T\textsubscript{anneal} (C) | t\textsubscript{anneal} (h) | $\beta$ Fe\textsubscript{x}Se\textsubscript{y} (%) | $\delta$ Fe\textsubscript{3}Se\textsubscript{4} (%) | $\alpha$-Fe (%) | Other |
|--------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|--------|
| 1      | 1.14:1          | 1.66            | 750             | 23              | NA              | NA              | 77              | 14              | 9      |
| 2\textsuperscript{*} | 1.14:1          | 1.66            | 750             | 44              | NA              | NA              | 78              | 18              | 5      |
| 3\textsuperscript{*} | 1.06:1          | 1.66            | 600             | 200             | NA              | NA              | 76              | 22              | 2      |
| 4      | 1.06:1          | 1.66            | 600             | 45              | NA              | NA              | 78              | 19              | 3      |
| 5      | 1.06:1          | 1.66            | 600             | 15              | NA              | NA              | 80              | 17              | 3      |
| 6      | 1.06:1          | 1.66            | 570             | 15              | NA              | NA              | 77              | 20              | 3      |
| 7      | 1.03:1          | 1.66            | 570             | 15              | NA              | NA              | 79              | 20              | 1      |
| 8      | 1.03:1          | 1.66            | 480             | 15              | NA              | NA              | 76              | 23              | 1      |
| 9\textsuperscript{**} | 1.03:1          | 1.66            | 480             | 15              | NA              | NA              | 75              | 25              | -      |
| 10\textsuperscript{*} | 1.03:1          | 1.66            | 420             | 10              | NA              | NA              | 72              | 26              | 2      |
| 11\textsuperscript{*} | 0.95:1          | 0.33            | 720             | 24              | 420             | 24              | 58              | 42              | -      |
| 12\textsuperscript{*} | 1.00:1          | 0.33            | 720             | 24              | 420             | 24              | 81              | 19              | -      |
| 13     | 1.01:1          | 0.33            | 690             | 24              | 420             | 24              | 84              | 16              | 1      |
| 14\textsuperscript{*} | 1.02:1          | 0.33            | 690             | 24              | 420             | 24              | 96              | 3               | -      |
| 15\textsuperscript{*} | 1.03:1          | 0.33            | 690             | 24              | 420             | 24              | 91              | 8               | -      |
| 16     | 1.03:1          | 1.66            | 410             | 15              | NA              | NA              | 57              | 41              | 2      |
| 17     | 1.03:1          | 1.66            | 360             | 10              | NA              | NA              | 57              | 37              | 1.5    |
| 18\textsuperscript{*} | 1.03:1          | 1.66            | 330             | 10              | NA              | NA              | 60              | 37              | 3      |
| 19     | 1.03:1          | 1.66            | 330             | 5               | NA              | NA              | 27              | 68              | 4      |
| 20     | 1.03:1          | 1.66            | 320             | 5               | NA              | NA              | 21              | 75              | 4      |
| 21\textsuperscript{*} | 1.01:1          | 1.66            | 330             | 5               | NA              | NA              | 21              | 73              | 5      |
| 22     | 1.01:1          | 1.66            | 300             | 5               | NA              | NA              | -               | 37              | 10     |
| 23     | Run 22          | 1.66            | 410             | 10              | NA              | NA              | 67              | 32              | 1      |
| 24     | Run 22          | 1.66            | 380             | 10              | NA              | NA              | 54              | 43              | 2      |

\textsuperscript{*} Samples used for EPMA study; \textsuperscript{+} based on Rietveld refinements of powder XRD data; \textsuperscript{**} This sample cooled down slowly over 45 h; ++ FeSe\textsubscript{2}; \textsuperscript{#} Fe\textsubscript{3}Se\textsubscript{4} (40%); FeSe\textsubscript{2} (12%).

In this study, the beam produced by a 15 kV and focused 30 nA source produces an electron beam-specimen total interaction volume of \(\sim 1\) \(\mu\)m as determined using the CASINO program [22] for modelling electron trajectories. However, the maximum depth of Fe K\(\alpha\) trajectories is \(\sim 200\) \(\mu\)m and that for Se L\(\alpha\) \(\sim 600\) \(\mu\)m. Given the average aggregate size of samples analysed, and the method of sample preparation, secondary x-rays generated from such depths are unlikely. Nevertheless, we estimate the average spot analysis using EPMA under these conditions is within a \(1\) \(\mu\)m radius of the beam location. Accompanying BSE and elemental x-ray maps by WDS used for phase analysis of individual powder particles on the electron microscope are conducted at 15 kV accelerating voltage, 30 nA beam current, focused beam and 40 or 80 ms dwell time per pixel in stage mode, using a step size of 200 \(\mu\)m.

Acquisition and image processing are obtained using the JEOL EPMA instrument and xCLent IV software. Single-pass maps are acquired simultaneously for back scattered electrons, K\(\alpha\) lines of C and Fe, and L\(\alpha\) for Se. The carbon x-ray signal is used in conjunction with BSE images to identify patches of conductive resin and to monitor contamination at grain margins. Images are subsequently processed using a 3 \(\times\) 3 averaging filter kernel, and a new variable defined by Se/Fe from wavelength-dispersive spectrometers, secondary and backscattered electron (BSE) detectors, Probe for EPMA [19] and xCLent IV software. Spot analyses on chalcogenides are performed using Fe K\(\alpha\) and Se L\(\alpha\) x-ray intensities measured simultaneously on LIFH and TAP analysing crystals, respectively, at 15 kV accelerating voltage, 30 nA beam current, and a fully focused beam. Pure metal standards are used for calibration and count times of 20 sec (peak and background) are used on unknowns for both elements. An exponential fit to the background positions of Se L\(\alpha\) is used to model the background intensity under the peak and a linear fit for the background under the Fe K\(\alpha\). Detection limits under these conditions are 0.025 weight percent (wt %) for Fe and 0.032 wt % for Se, with analytical sensitivity of 0.22% relative for both elements at the 99% confidence level.

The combined ZAF and $\phi_\rho z$ corrections of the Armstrong/Love-Scott quantitative analysis correction procedure [20] along with the LINEMU database [21] of mass absorption coefficients are used for EPMA data reduction in the Probe for EPMA software. Analyses with wt % greater than 101.0% or less than 99.0% are rejected during data compilation. In all cases, the wt% element totals average 99% or greater with average standard deviations <0.5 wt% per element.
the processed images. Thresholds of 20 or 40 counts for carbon (corresponding to 40 ms or 80 ms dwell times) per pixel are selected as cut-offs for edge effects, contamination or resin, based on inspection of x-ray counts in smooth grain interiors. Consistent thresholds for Sc/Fe in all samples are also defined that differentiate the two Fe₄Se₃ phases previously identified by WDS quantitative spot analysis and BSE contrast. Together these criteria define ≥ 99.5% pixels as resin, contaminated cracks and edges or Fe₄Se₃ phases. Phase proportions derived from the pixels that pass the filtering criteria for Fe₄Se₃ are compared with BSE images.

Compositions for iron selenides are variously reported in the literature with designations such as Fe₁₊ₓSe, Fe₁₋ₓSe, FeSe₁₋ₓ, Fe₂Se, and in order to designate non-stoichiometry or the presence or absence of defects or vacancies [10, 23]. In this work, we use the formalism Fe₄Se₃ to denote composition of all synthesized selenide compounds. We convert the stoichiometry for Fe₄Se₃ compounds reported in the literature to the same formalism in order to provide consistency to the narrative.

Zero field cooled (ZFC) and field cooled (FC) magnetisation curves as a function of temperature are measured at 100 Oe using a Cryogenic Ltd Mini Cryogen-free System (Cryogenic Ltd, London, UK) with a 5 T magnet. Tc, was determined as the intersection of the linearly extrapolated M(T) with the M = constant line. For comparison of magnetisation data, we normalised the weight of each sample.

3. Results

We present a selection of experimental data to demonstrate the range of conditions for which high yields of tetragonal β-Fe₄Se₃ may form. Table 1 presents data for reactions that result in formation of β-Fe₄Se₃ as the major phase in powder products (e.g. >50%) as well as examples in which β-Fe₄Se₃ is not the major phase or is not present as determined by XRD Rietveld refinement. In general, reactions for which β-Fe₄Se₃ is the major phase are for maximum temperature, T_max, above 330 °C with a sintering time, t_hold, for 10 h or more. Reactions that produce β-Fe₄Se₃ in lesser proportion to β-Fe₄Se₃ or other phases occurs for T_max ≤ 330 °C with a sintering time, t_hold, less than 10 h.

3.1. Iron chalcogenide syntheses

Table 1 describes generic variables that affect the relative proportion of iron selenide products especially β-Fe₄Se₃. Table 1 provides outcomes for (a) variation in T_max with different starting ratios, (b) differences in hold time, t_hold, for similar starting ratios and (c) variation in starting ratios of Fe and Se for similar T_max and t_hold. Table 1 shows that tetragonal β-Fe₄Se₃ forms after heating to a wide range of temperatures (∼330 °C to ∼750 °C), and a wide range of starting compositions (0.95 < x < 1.14).

Reactions with similar ratios of starting materials (e.g. Runs 1–2; 3–6; 7–10), show relatively high proportions of tetragonal phase (e.g. >70%) over a wide range of hold times (e.g. 10 h to 200 h) at all temperatures above 420 °C. An increase in temperature for the same starting ratio and hold time (e.g. Runs 7–8), improves yield of β-Fe₄Se₃ marginally and, within experimental error, increases the proportion of hexagonal δ-Fe₄Se₃, presumably due to conversion of excess α-Fe. The amount of α-Fe in the products from these reactions determined by XRD is very low; sufficient to indicate presence. Examination of products from reactions with similar T_max and starting ratios, suggests that a longer hold time may result in a lower amount of α-Fe (e.g. Runs 1–2; 3–6; 9–10) with concomitant increase in either β-Fe₄Se₃ or δ-Fe₄Se₃. Furthermore, XRD data for Run 9 show that no α-Fe is present and is likely due to the very slow cooling rate from 480 °C to room temperature (i.e. 45 h).

Formation of β-Fe₄Se₃ phase is also critically dependent on small changes in the ratio of Fe:Se for starting compositions as indicated by Runs 11–15. A maximum yield of 96% β-Fe₄Se₃ is obtained for Run 14 with starting ratio for Fe:Se = 1.02: 1, T_max = 690 °C and t_hold = 24 h, with subsequent in situ annealing at 420 °C for 24 h. Slight changes to the ratio of Fe:Se affects the proportion of final products as shown for Runs 11–15 (table 1). For example, Runs 14 and 15 show >90% of β-Fe₄Se₃ in the final product when sintered above 690 °C—a significant increase compared with Runs 11–13. Notwithstanding the relative error for Rietveld refinements of powder XRD data, we suggest the improved yield for Runs 14 and 15 are due to the higher Fe ratio of the starting materials.

Excess Se in Run 11 results in formation of a higher amount of δ-Fe₄Se₃ phase in the final product compared with all other syntheses in table 1. However, excess iron in the starting materials is favourable for formation of β-Fe₄Se₃. A lower heating rate for similar reaction conditions, in particular, with excess iron in starting ratios suggests that less α-Fe is formed in the final product (c.f. Runs 12–15 with Runs 1, 3 and 5).

Products resulting from variations in T_max for Fe:Se = 1.03 and 1.01 and differences in the hold time at lower T_max values are summarized in table 1. For example, a reduction of sintering time from 10 h to 5 h for 300 °C < T_max < 330 °C changes the proportion of β-Fe₄Se₃ significantly (Runs 17–22). However, re-heating Run 22 to 410 °C and 380 °C, respectively, results in the formation of β-Fe₄Se₃ as a predominant phase (Runs 23 and 24). Other phases present at T_max = 300 °C, results in formation of Fe₃Se₄, FeSe₂ and α-Fe.

3.2. Phase chemistry

We list in supplementary information (table S1) average compositions from selected phases within aggregates from thirteen separate reactions in the Fe–Se phase field investigated. Each average composition, based upon identification of the bright and dark regions using BSE images, is determined from the number, n, of point (or spot) analyses listed in table S1. The 255 separate point analyses obtained by the EPMA and compiled in table S1 are a subset of the >300 analyses undertaken on Fe and FeSe samples. Standard deviations
of average analyses are calculated using conventional statistics for each image contrast region. Based on these EPMA analyses, the darker image contrast regions of BSE images are Fe-rich while the brighter image contrast corresponds to Se-rich regions. For bright BSE contrast, Fe concentrations vary by \( \sim 2.9 \) wt% and Se concentrations vary by \( \sim 1.8 \) wt%. For darker BSE image contrast, Fe concentrations vary by \( \sim 4.2 \) wt% and Se concentrations vary by \( \sim 2.3 \) wt%.

3.3. Morphology and microstructure

Figure 1 shows typical products from Run 9 as polished aggregates using three complementary imaging techniques. The BSE image of the products from Run 9 (figure 1(a)) shows that the product aggregates contain two different phases as indicated by the bright and dark grey image contrast that typically corresponds to variations in atomic number.

Image analysis of the colour-coded grains in figure 1(b) calculate relative proportions of 25% for green and 75% for blue segments. These values compare with 25% for \( \delta \)-Fe\(_x\)Se and 75% for \( \beta \)-Fe\(_x\)Se determined by Rietveld refinement of XRD data (table 1). Similar correlations of the bright and dark grey BSE images with relative proportions of \( \delta \)-Fe\(_x\)Se and \( \beta \)-Fe\(_x\)Se, respectively, are observed for samples from other reactions.

The EBSD image and Euler map in figures 1(c) and (d), respectively, confirm the crystal orientation and structure of the sample from Run 9 using known crystallographic data for \( \beta \)-Fe\(_x\)Se and \( \delta \)-Fe\(_x\)Se. Figure 1(c) shows that the two phases, \( \beta \)-Fe\(_x\)Se and \( \delta \)-Fe\(_x\)Se are major phases in the product from Run 9. This determination is in good agreement with XRD results for this sample (as indicated in table 1) as well as with combined WDS mapping and BSE imaging. The Euler map in figure 1(d) shows that individual grain orientations in this aggregate are, in general, random with limited preferred orientation.

We present further examples of aggregates from Runs 4, 5 and 14 in supplementary information (figures S1–S3 (available online at: https://stacks.iop.org/SUST/33/075003/mmedia)). For Runs 14 and 15, we show good agreement between EBSD, WDS mapping and XRD results and tabulate these data for...
three typical experimental runs in Table 2. Based on these data, we conclude that the darker BSE image contrast areas correspond to the $\beta$-Fe$_2$Se phase and that the brighter BSE areas correspond to $\delta$-Fe$_2$Se on polished sections as exemplified in figures 1, S1 and S2.

Figure 2 compares unannealed samples sintered at 480 °C for 15 h (Run 8) with that of aggregates that have been sintered at 720 °C and then annealed at 420 °C for 24 h (Run 11). In the latter case, both types of Fe$_2$Se phases are larger than phases sintered for shorter times (e.g. Run 8). However, unlike previous studies which have not focused on microstructure, note the presence of both $\beta$-Fe$_2$Se and $\delta$-Fe$_2$Se in these images.

Figure 3 compares microstructures for samples prepared at lower temperature and highlights the effect of sintering time. In this case, an additional 5 h sinter substantially increases grain sizes within aggregates and shows enhanced growth of $\beta$-Fe$_2$Se. Critically, for an understanding of phase relationships, both $\beta$-Fe$_2$Se and $\delta$-Fe$_2$Se are present when sintered from starting powders at these lower temperatures, albeit in different proportions. In addition, nano-scale particles with a high brightness BSE signal that surround aggregates and are within void regions (e.g. containing epoxy or remnant Fe), are inferred to be remnant liquid Se that has solidified on cooling.

These high brightness particles are much less abundant, or absent, in samples prepared at higher temperature with longer sintering and/or annealing times. Furthermore, at lower sintering temperatures the presence of unreacted Fe can be readily observed using high contrast BSE images (e.g. figure S4, supplementary information).

### 3.4. Magnetic measurements

Superconductivity was observed for all samples with predominant $\beta$-Fe$_2$Se phase (e.g. > 70%) within the range 6.8 K $\leq$ T$_c$ $\leq$ 8.2 K as summarised in supplementary information (table S2). A selection of $\beta$-Fe$_2$Se samples have been evaluated using magnetic measurements. Figure 4 illustrates the temperature dependence of magnetization in both ZFC and FC modes at an applied field of 100 Oe for samples from Run 14. The normal state is characterized by a positive magnetization that increases with increasing amount of hexagonal $\delta$-Fe$_2$Se and residual iron phase in as-prepared samples.

Samples from Runs 14 and 15 with $\beta$-Fe$_2$Se phase present at >90% exhibit superconductivity at T$_c$ = 7.6 K and 7.5 K, respectively. The T$_c$ values of samples from different synthesis runs are provided in supplementary information (table S2). The highest T$_c$ value obtained for these samples is for Run 3 at 8.2 K. Samples from this run contain $\sim$20% $\delta$-Fe$_{0.92(1)}$Se and $\sim$76% $\beta$-Fe$_{1.02(1)}$Se.

### 4. Discussion

The stoichiometry of Fe$_2$Se phases in the proximity of Fe:Se = 1:1 is key to an understanding of superconductivity in the chalcogenide suite of materials [2, 10, 23]. In this work, we have utilised a different and direct approach to statistically determine stoichiometry on an individual grain-by-grain basis for the synthesized product(s). The spatial and chemical precision in this study enables interpretation that complements similarly precise studies on bulk samples using high resolution neutron diffraction [10, 13]. We place emphasis on previous studies that have analyzed the composition or stoichiometry of final products from a reaction rather than an assumed composition based on the ratio of starting materials.

#### 4.1. Synthesis of Fe$_2$Se

Synthesis conditions used in this study are similar to that described as LTS (low temperature synthesis) by Pomjakushina et al [13] and extend upon conditions described by Grivel [11]. Figure 5 shows typical heating and cooling profiles for reactions using powdered starting materials of Fe and Se by McQueen et al [10], Grivel [11] and this work. The liquid and gas phase transition temperatures for elemental Se (221 °C and 685 °C, respectively) are also shown as pink dotted lines in figure 5.

The profile representing experiments by McQueen et al [10] are described as high temperature synthesis[13] and are directed at obtaining phase pure $\beta$-Fe$_2$Se product without $\delta$-Fe$_2$Se or $\alpha$-Fe. In these experiments by McQueen et al [10] and earlier predecessor studies [24], the Se reactant is substantially in the gaseous state. For a range of synthesis conditions at lower temperatures, Grivel [11] shows that the predominant $\beta$-Fe$_2$Se phase has an iron-rich stoichiometry (i.e. Fe$_{1.01}$Se to Fe$_{1.02}$Se). This stoichiometry was determined by large-area (i.e. $\sim$20 μm$^2$) average analysis using an SEM/EDS on polished samples. In the study by Guo et al [12], the stoichiometry of $\beta$-Fe$_2$Se that produces maximum T$_c$ was estimated to vary between 1.0 < x < 1.02, for samples with minimal presence of other phases.

In this work, we combine sintering and annealing in the one reaction chamber in order to minimize the influence of oxygen in a two-step grinding/sintering/annealing process [10]. Exceptions to this approach are Runs 23 and 24 of table 1. In these examples, we show that a complex mixture of FeSe phases synthesized at low temperature, for short sintering periods (5 h) at 300 °C may be converted to $\beta$-Fe$_2$Se by re-sintering at 380 °C or 400 °C for 10 h. Our study departs from the syntheses by Onar and Yakinci [25], some experiments by

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**Table 2.** Relative phase proportions determined by three analytical techniques.

| Run No. | XRD $\beta$-Fe$_2$Se (%) | EBSD $\beta$-Fe$_2$Se (%) | WDS mapping (EPMA) | Dark (%) | Bright (%) |
|---------|--------------------------|--------------------------|-------------------|----------|-----------|
| 9       | 75                       | 25                       |                   | 75       | 25        |
| 14      | 96                       | 3                        |                   | 97       | 3         |
| 15      | 91                       | 8                        |                   | 92       | 8         |

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Figure 2. Microstructures using BSE imaging for (a) Run 8 sintered at 480 °C for 15 h without annealing and (b) Run 11 sintered at 720 °C for 24 h and annealed at 420 °C for 24 h. Red circles indicate locations for EPMA analyses. Note the larger size and euhedral definition for grains of both FeSe phases in (b).

Grivel [11] and by Gawrylak et al [14], in which sintering is a two-step process. In these works and this study, reactions are predominantly below the transition temperature at which elemental Se is a gas.

A recent in situ synchrotron study on similar starting materials to this study clearly demonstrates that Se is substantially in liquid form above 260 °C and reacts with Fe to form FeSe solids at higher temperatures [24]. Gawrylak et al [14] also performed syntheses in which starting materials are held at 1085 °C for 24–48 h with subsequent slow (3 °C hr⁻¹ to 1020 °C) and long period (>24 h) cooling regimes to 340 °C prior to quenching. Samples produced by this process resulted in proportions of β-Fe₅Se ranging from 61% to 78% in the final product and Tc ranging from 8.5 K to 6.3 K [14]. Of significance is the extensive annealing periods at 340 °C. In other syntheses, Gawrylak et al [14] noted that proportions of β-Fe₅Se in products sintered at 700 °C remained low (52% to 58%) except for samples sintered at 750 °C with annealing at 340 °C.

Similar trends for sintering and annealing temperatures are evident from the data provided in table S1 (supplementary...
information) of this study. For example, without lower temperature annealing at 420 °C or below, all samples sintered at higher temperatures up to 750 °C show proportions of β-Fe$_3$Se ranging from 72% to 80% even with reaction times up to 200 h (Runs 1–10). In some cases, such as Runs 7–9, low amounts, or absence of, α-Fe in the product (determined by XRD) shows limited impact on the relative proportion of β-Fe$_3$Se in the final product. Nevertheless, lower temperature sintering at 360 °C and 330 °C for 10 h without annealing produces ∼60% of β-Fe$_3$Se (Runs 17 and 18, table 1) in addition to δ-Fe$_5$Se$_2$ and α-Fe and, in one case, FeSe$_2$.

Table 1 shows that samples synthesized from a range of starting compositions (0.95 < Fe:Se < 1.03) when annealed for 24 h at 420 °C result in formation of β-Fe$_3$Se as primary phase. Sintering at ∼690 °C to 750 °C with annealing at 420 °C results in high yields (> 80%) of β-FeSe. Similar to observations in previous studies [10, 13], excess Fe in the starting composition enhances formation of β-Fe$_3$Se (Runs 14 and 15; table 2).

Collectively, the data from these syntheses suggests a link between sintering and annealing temperatures to obtain maximum yield. For example, Pomjakushina et al [13] obtain maximum yield of 98.3(6)% for β-Fe$_{1.02}$ after sintering at 700 °C and annealing at 400 °C. On the other hand, using a similar process Gawryluk et al [14] obtained maximum yield of 96% with sintering and annealing temperatures of 750 °C and 340 °C, respectively. From our syntheses shown in table 1, the maximum yield of β-Fe$_{1.02}$ occurs at sintering and annealing temperatures of 690 °C and 420 °C, respectively.

While the precise conditions for maximum yield of β-Fe$_3$Se in a single step process without the presence of any impurity is still elusive, diffusion processes define the Fe$_3$Se microstructure and resultant superconducting properties of orthorhombic FeSe. Evidence for the efficacy of diffusion processes in the formation of β-FeSe is elegantly provided by Wang et al [26]. In this work, mm-scale tablets of β-FeSe are produced by immersing an iron block in excess Se liquid at 650 °C for periods of 100–150 h and then annealing at 400 °C for 24 h [26].

On a smaller scale, diffusion mechanisms are also invoked to explain the sequential formation of FeSe phases, and ultimately, β-Fe$_3$Se from elemental starting materials [24] as well as in fast combustion synthesis [27]. In these examples, the reaction between solid Fe and liquid Se occurs at the interface of these phases and is limited by the diffusion of atoms at that interface. Accordingly, Se-rich phases such as FeSe$_2$ and Fe$_3$Se$_2$ form first at the interface [24, 27] and is evident for low temperature reactions shown in table 1 (Runs 17 and 18). At higher temperatures, diffusion occurs more rapidly (even though the solubility of Fe in liquid Se is close to zero; 0.04 atom % at 790 °C [9]) and FeSe phases form.

4.2. Microstructure of Fe$_3$Se Phases

Contrast mechanisms derived from electron-solid interactions are well known [28] and have been used in this work to identify Fe$_3$Se phases produced by the example reactions listed in table 1. Correlation of backscattered images with spatially precise EPMA elemental analyses confirms the identification of both β-Fe$_3$Se and δ-Fe$_5$Se in polished samples from these experiments. There are few other studies on the microstructure of Fe$_3$Se phases, particularly those formed by reactions similar to those listed in table 1. Furthermore, congruent spatial interpretation by three separate imaging techniques from polished sections of Runs 9, 14 and 15 and other samples (not shown) provides a high level of confidence regarding microstructural interpretations.

The SEM + EDX analyses of Onar and Yankinci [25] are of insufficient resolution and grain size to discern similar subtleties in microstructure as noted above in figures 2 and 3. The study by Grivel [11] is the only other in which polished section(s) of products are examined using BSE and SE images. Figures 3 and 7 of Grivel [11] show similar microstructures to that observed in figures 1 and 2 of this work although at different magnifications. Careful attention to their BSE images suggests image contrast similar to figure 1(a) may
be present, albeit resolution is not high and grain size contrast is indeterminate.

The microstructure of un-annealed samples cooled from their sintering temperature as shown in figure 1 and listed in table 1 show that two phases, $\beta$-Fe$_x$Se and $\delta$-Fe$_x$Se, co-exist within large aggregates. Similarly, the microstructures for annealed samples cooled from a range of sintering temperatures show similar characteristics and clearly show that two phases, $\beta$-Fe$_x$Se and $\delta$-Fe$_x$Se, co-exist within large aggregates and are connected via interfacial boundaries. With a higher proportion of $\beta$-Fe$_x$Se determined by XRD (e.g. Run 14; figure 2), image contrast is consistent across many aggregates and the presence of $\delta$-Fe$_x$Se is uncommon.

EBSD maps are useful tools to validate microstructural interpretations based on image contrast because their character depends on elastically scattered BSEs that have undergone coherent Bragg scattering as they leave the specimen [29, 30]. Figure 1(c) shows the relative proportions of $\beta$-Fe$_x$Se ($\sim$70%) and $\delta$-Fe$_x$Se ($\sim$30%) in Run 9 based on cell dimensions and also the orientations of individual grains within the aggregate (figure 1(d)). In this case, grain orientations are randomly defined for either phase of Run 9 in comparison to the Euler map for Run 14 (figure S1(d); supplementary information) which shows a higher proportion of preferred grain orientations for $\beta$-Fe$_x$Se.

4.3. Stoichiometry of Fe$_x$Se

The stoichiometry of FeSe phases and the presence of defects, interstitial ions has been subject to ongoing discussion since early phase relation and structural studies by Svendsen [31] and others. As noted by Svendsen [31], these structures generally show iron vacancies as the Se content increases. Neutron diffraction studies by McQueen et al [10] and Pomjakushina et al [13], clearly demonstrate non-stoichiometric $\beta$-Fe$_x$Se occurs in reaction products.

Recent TEM and Selected Area Electron Diffraction (SAED) studies on zero, one and two dimensional $\beta$-Fe$_x$Se identified three types of iron vacancy ordering in a tetragonal lattice [23]. This study also excluded the possibility of ordering of Fe interstitials and Se vacancies in each ordered superlattice structure. These findings support earlier suggestions that compositional variations in the FeSe system near 50:50 ratios are predominantly due to iron vacancy ordering [31].

We use two approaches to estimate the stoichiometry of FeSe phases in these reaction products. Firstly, for Runs 9, 11, 12 and 14, additional XRD patterns were obtained using longer collection times and an internal corundum standard for calibration of peak positions. These data are used to refine cell dimensions and Se occupancy for each FeSe phase identified by previous Rietveld analysis. Secondly, for the reactions listed in table S1 (supplementary information), detailed EPMA analyses provide spatially precise compositions of individual grains within an aggregate.

4.3.1 XRD Refinement. Two refinement methods are evaluated using additional XRD data for Runs 9, 11, 12 and 14: (a) refined Se occupancy and cell parameters and (b) refined cell parameters using Se occupancies assigned by EPMA data shown in table S1 (supplementary information). For method (a), we calculated the best fit of diffraction data in two stages based on the weighted R factor: (i) cell dimension refinements while Se occupancy is fixed at 0.95 and at 1.0 respectively and (ii) refinement of Se occupancy based on best fit of cell refinement. These data show a wide range of Se occupancy and $R_{wp}$ values as shown in supplementary information (table S5).

For method (b), supplementary information (table S6) shows the starting Fe:Se ratios for each synthesis, as well as the experimentally determined values for Se occupancy using EPMA. These refinements show strong correlation of cell dimensions with reaction temperature for $\beta$-Fe$_x$Se and also for the complementary $\delta$-Fe$_x$Se phase in the product even when in low abundance. The standard errors determined for $\delta$-Fe$_x$Se in Run 14 are significantly higher than other refinements due to the poor XRD signal for this phase ($\sim$3% present; table 1). Linear regression analysis of the Se cell dimension variation with sintering temperature for $\beta$-Fe$_x$Se gives an $R^2 = 0.997$ and similarly, for $\delta$-Fe$_x$Se, $R^2 = 0.995$. In both cases, $c$ axis refinements show a greater variation with $T_{\text{max}}$ for which $R^2 = 0.81$ for $\beta$-Fe$_x$Se and $R^2 = 0.85$ for $\delta$-Fe$_x$Se. The $a$ axes for $\beta$-Fe$_x$Se and $\delta$-Fe$_x$Se show opposite trends with sintering temperature (figure S5; supplementary information).

McQueen et al [10] show that the ratio $c/a$ for unit cell parameters of $\beta$-Fe$_x$Se correlate with $T_x$ in samples prepared at low temperature or with lower iron content. Samples with $c/a \sim 1.464$ or above show the highest values for $T_x$ while samples with values near 1.461 (and $x = 1.03$) do not show superconductivity [10]. The $c/a$ ratios for $\beta$-Fe$_x$Se samples shown in table S6 are at or near 1.464 as well as for all ratios obtained using other formats for XRD refinements noted above (tables S3–S5; supplementary information). All $\beta$-Fe$_x$Se evaluated in this study using magnetization measurements showed a superconducting transition.

4.3.2 Elemental Analyses. Similar to spatially precise electron diffraction studies that enable collection of crystallographic data from individual grains, use of spatially precise EPMA and EBSD data provides clarity on both the composition and structure of individual grains in the Fe:Se system. The analyses listed in table S1 (supplementary information) as well as shown in figures 1–3 and figures S1 and S2 show that two distinctive phases form within a narrow composition range.

Data on $\beta$-Fe$_x$Se stoichiometry suggests that even with substantial differences in starting ratios of Fe:Se as elemental powders, a tendency to drive the ratio of Fe:Se toward excess Fe in the final tetragonal product occurs for syntheses over a wide range of temperatures with and without annealing. This tendency is illustrated in figure 6 in which initial Fe:Se ratios are plotted on the ordinate for reactions from this work (red circles) as well as those of McQueen et al [10] (green diamonds) and Pomjakushina et al [13] (blue squares) against x.

The data by McQueen et al [10] and Pomjakushina et al [13] are based on refinements of neutron diffraction (ND) data.
for the $\beta$-Fe$_x$Se phase only. With few exceptions, Fe:Se starting ratios varying by up to 20% (either side of Fe:Se = 1.0) will tend towards formation of $\beta$-Fe$_x$Se with a variation in estimated stoichiometry of less than 4%. This trend emphasises the conclusions by others [10, 13] that the properties of FeSe compounds are very sensitive to composition and order/disorder. In addition, these data show that a stable equilibrium phase in this system, with or without the presence of other Fe or FeSe phases, is $\beta$-Fe$_x$Se.

The heating/cooling profile for Run 14 resulted in the highest proportion of $\beta$-Fe$_x$Se in the product at 96% ± 4%. The stoichiometry of this phase determined by EPMA is $\text{Fe}_{1.02\pm0.001}\text{Se}$ (table S1; supplementary information). This value is consistent with the optimum composition of $\text{Fe}_{1.020\pm0.000}\text{Se}$ (translating to consistent nomenclature) [13] and at Fe$_{1.01\pm0.02}$Se [10] determined using neutron diffraction.

However, a substantial difference in the reaction products between the study by Pomjakushina et al [13] and this work relates to the proportion and type of secondary, or minor, phases. Relatively high proportions of $\alpha$-Fe (up to 12.5%) and relatively low proportions of $\delta$-Fe$_x$Se by Rietveld refinement are reported [13] in comparison to lower proportions of $\alpha$-Fe in this work. Where the proportions of both $\alpha$-Fe and $\delta$-Fe$_x$Se are low [13], $\beta$-Fe$_x$Se is at the optimum composition noted above. Similarly, the optimum yield of $\beta$-Fe$_x$Se shows an iron-rich stoichiometry at Fe$_{1.02\pm0.001}$Se in this work.

Superconductivity was observed for all samples with predominant $\beta$-Fe$_x$Se phase (e.g. >70%) within the range 6.8 K ≤ $T_c$ ≤ 8.2 K. The normal state is characterised by a positive magnetization that increases with increasing hexagonal $\delta$-Fe$_x$Se and residual iron phase. This contribution is large enough to prevent magnetization with negative values to 2 K for samples from Runs 1–13. However, samples from Runs 14 and 15 with $\beta$-Fe$_x$Se as a major phase exhibit superconductivity at $T_c$ = 7.6 K and 7.5 K, respectively. Normal state magnetization is close to zero for samples from Runs 14 and 15, as can be expected from a decreased amount of $\delta$-Fe$_x$Se and residual Fe phases compared to other samples. This outcome shows that improvement of superconducting properties is dependent on optimization of reaction time, temperature and in situ annealing in order to attain an appropriate stoichiometry. Samples that are not annealed at 420 °C show higher positive background values for magnetization due to higher levels of magnetic impurity phases.

4.4. Phase boundaries at Fe:Se ~ 1

According to early studies of the FeSe system, the tetragonal phase undergoes a peritectoid reaction with formation of $\delta$-FeSe and iron at 458 °C [31]. A more recent compilation of thermodynamic data by Okamoto [9] suggests that the peritectoid temperature is either higher than 650 °C or that $\delta$-FeSe completely transforms to $\beta$-FeSe. Okamoto [9] encouraged resolution of this ambiguity for $\beta$-FeSe and this has been a consideration of some studies since discovery of the orthorhombic SC FeSe [2]. In addition, this early work proposed that the $\beta$-FeSe form exists on the Fe-rich side of FeSe stoichiometry with a homogeneity range from 49.0 to 49.4 atom% Se [9] (i.e. 51.0 to 50.6 atom % Fe; or $\Delta x = 0.017$). Subsequently, a narrow compositional range for $\beta$-Fe$_x$Se has been proposed by a number of researchers [2, 10, 13, 32].

McQueen et al [10] propose that the tetragonal $\beta$-Fe$_x$Se phase is not stable above 455 °C nor below 300 °C [10]. Instability above 455 °C appears to confirm the suggestion by Okamoto [9] and Svendsen [31] that a peritectic transformation occurs above this temperature. However, experiments by others [11–14, 24] and this study at temperatures up to 750 °C show that $\beta$-Fe$_x$Se forms above 455 °C. In many cases, formation of $\beta$-Fe$_x$Se is accompanied by one other phase (e.g. $\alpha$-Fe or $\delta$-FeSe) at these higher temperatures. Even with secondary phases present, $\beta$-Fe$_x$Se also results in transformation to the orthorhombic SC form when cooled below 9 K [11, 13] and as shown in this study. The presence of secondary phases such as $\alpha$-Fe and/or $\delta$-Fe$_x$Se influences overall physical properties at low temperature but may not extinguish superconductivity.

4.4.1. Microstructure and FeSe compositions. We show in figure 7 spatially and compositionally precise data for phases obtained from reactions with different sintering temperatures (and times) and with/without annealing as listed in table 1. Figure 7 shows compositions for hexagonal (yellow circles) and tetragonal (aqua squares) forms of Fe$_x$Se. Figure 7 also identifies reactions that include annealing at 420 °C for 24 h (dark blue squares and green hexagons) which lie within the same compositional range as sintered samples without annealing. Within the errors determined from multiple analyses of both phases present in each reaction product, there is a clear compositional separation of the $\beta$-Fe$_x$Se and $\delta$-Fe$_x$Se components. This compositional trend with temperature of formation, as well as the microstructures (figures 1–3), confirm that these phases co-exist within this temperature range.
Figure 7. Plot of experimentally determined phase compositions for the Fe–Se system (this work). Data for this plot are in Supplemental Information (table S1). For each data point, the relevant Run number (table 1) is designated ‘Rn’. β-Fe₅Se is designated by squares, δ-Fe₅Se is designated by hexagons.

At these temperatures, β-Fe₅Se will be stable and, as shown in figure 7 and by ND studies [13], will adopt a composition within a very narrow range (±2 atom%). This strong tendency to form β-Fe₅Se within a narrow composition range, is consistent with data shown in figure 6. For similar sintering temperatures (e.g. ∼690 ºC), annealing reveals a potential dependence on starting ratios of Fe:Se, particularly in the value of x for δ-Fe₅Se (c.f. Runs 14 and 15). Further data is required to fully evaluate this aspect of FeSe phase formation. The precise level and degree of vacancy ordering within β-Fe₅Se will then depend on processing conditions such as sintering and annealing temperatures and times. Clearly, slight variations in processing conditions may give rise to substantial shifts in superconducting properties as previously noted [11, 23].

4.5. Revised phase diagram

Figure 8 shows extracts from Fe–Se phase diagrams developed for the region Fe:Se ~ 1 based on earlier studies and this work. Both diagrams in figure 8 identify the location of the single experiment (yellow diamond) undertaken by Grønvold [33] that suggests a peritectic for β-Fe₅Se at 457 ºC for x = 1.04. In the same report, Grønvold [33] notes a transformation from tetragonal FeSe as the major phase to hexagonal FeSe between 440 ºC and 465 ºC for x = 1.08 (i.e. 52 at % Fe). Special care was taken during these experiments to eliminate loss of elements during a reaction [33]. However, the precise elemental composition of the equilibrium products is unclear and may be based on an assumption that the stoichiometry is equivalent to the ratio of initial starting materials. As noted above, such an assumption may not be valid.

Figure 8(a) is a segment of the phase diagram for Fe–Se constructed by Okamoto [9] based on calorimetric, Mossbauer and crystallographic data on samples synthesised prior to 1990. These data define the upper limits of the phase diagram (e.g. liquidus boundaries) and, in general, are based on XRD studies of equilibrium reaction products. Detailed analysis of the compilation by Okamoto [9] suggests that few experiments...
have been performed in the region 500 °C < T < 750 °C for 1.5 < x < 0.92 (i.e. 60 at % Fe < x < 48 at % Fe). Key lines from the α-Fe end member are identified by experiment but the vertical boundary for α-Fe and δ-FeSe reproduced in figure 8(a) shows limited data [9].

The experiments by Pomjakushina et al [13] show that β-FeSe forms at 700 °C for 1.037 < x < 1.021 albeit in the presence of α-Fe and that these β-FeSe stoichiometries result in a superconducting compound when cooled below 9 K. A more recent interpretation of the Fe–Se phase diagram that incorporates recent experimental data on β-FeSe [10, 13] is provided for reference in supplementary information (figure S6). Figure S6 presents two views on the stability field for β-FeSe when annealed at 400 °C [13] and between 300 °C and 500 °C [10]. These views are the inferred phase boundaries by Pomjakushina et al [13] and that determined by McQueen et al [10]. According to McQueen et al [10], β-FeSe slowly converts to δ-FeSe below 300 °C.

Data from this study and a recent in-situ experiment using synchrotron XRD [24], suggests that β-FeSe forms via other FeSe phases (e.g. FeSe₂, Fe₂Se₃, and hexagonal γ-Fe₂Se₅) on heating Fe and Se powders from 25 °C to above 300 °C. Radiant cooling from ∼450 °C does not induce a phase change in the final products formed below 300 °C [24]. Differences in structural form of these FeSe compounds at low temperature may be due to substantial variations in annealing/cooling times and consequent ordering of interstitials or vacancies [10].

Earlier Mossbauer studies suggest that FeSe alloys with 4 to 25 at % Se (i.e. 96 to 75 at % Fe; outside the field of reference in figure 8(b)) when quenched from 500 °C to 650 °C, are two phase: α-Fe and β-FeSe [34]. This result is consistent with the data presented by Pomjakushina et al [13] at 700 °C and would suggest that the extent of β-FeSe may be greater than previously identified. Unfortunately, analyses of the final product(s) were not undertaken by Jain et al [34].

Figure 8(b) incorporates the results from experiments listed in tables 1 and S1 (supplementary information) and leaves open the nature of the phase boundary at ∼770 °C because our data do not extend to higher temperatures. The iron rich boundary β-Fe₅Se₇ aligns closely with the notional peritectic point at 457 °C previously identified [10, 31]. For reference, we re-plot in supplementary information (figure S7) the data from figure 7 with the stoichiometric values for β-Fe₅Se₇ determined by Pomjakushina et al [13].

Using the sintering temperature for these data [13] and the proportions of minor phases present in the final product, we annotate in figure 8(b) a boundary between the two phase regions at x ∼ 1.02 (i.e. ∼50.5 atom % Fe) where α-Fe becomes a predominant minor phase. We propose a two-phase field for β-Fe₅Se₇ and α-Fe for 457 °C < Tₘ < 700 °C for x > 1.02 and locate a tentative phase boundary at x = 1.08 (i.e. 52 at % Fe). While we have not explored this region of the phase diagram in detail, we suggest that the extent of this β-Fe₅Se₇ and α-Fe two phase field also extends to lower temperatures (below the 457 °C line) [9]. As shown in figures 7 and 8(b), the two-phase field for β-Fe₅Se₇ and δ-Fe₅Se₇ is positioned between 1.02 < x < 0.90.

Contrary to earlier studies [10, 12, 13], the data in figure 7 suggest that β-Fe₅Se₇ may also form on the iron-poor side of the phase diagram. Okamoto [9] notes in the description of phase boundaries for δ-FeSe, that an unusual eutectoid reaction at 53.3 at % Se (i.e. 48.7 atom % Fe) is, in essence, the transformation of δ-FeSe to β-FeSe + δ-FeSe that occurs at 350 °C. The Se-rich boundary of this two-phase region is shown in figure 8(b) to ∼47 atom % Fe (i.e. ∼53 atom % Se). The data shown in figure 7 for x ∼ 0.90 (i.e. 47.5–47.0 at % Fe) at ∼330 °C to ∼750 °C adds support to this earlier interpretation of the Fe–Se phase diagram [9].

Finally, we have no data from this study on the composition nor microstructure of phases for x > 1.02 and at temperatures below 457 °C. Hence, we propose that this region of the phase diagram requires further investigation. We also recognise that more precise methods of analysis may shed further light on the specific nature of the peritectic described in early literature [9, 10, 13, 33].

5. Conclusions

Previous work on the synthesis of β-Fe₅Se₇ the precursor phase that transitions to an orthorhombic SC phase below 9 K, identified a narrow range of x values for optimum yield (i.e. ∆x = 0.017). In this work, syntheses under non-oxidising conditions between 300 °C and 750 °C for a range of Fe:Se ratios of starting elements, show that β-Fe₅Se₇ forms over a wider range of x values (i.e. ∆x = 0.06; or ∼1.5 at %) and temperatures in a two-phase field with δ-FeSe. A second two-phase field for β-Fe₅Se₇ with α-Fe (∆x ∼ 0.02) at temperatures >460 °C, and possibly lower, is inferred from previous studies [13] for ∼1.02 < x < ∼1.04. These syntheses are undertaken at temperatures that invoke, or are limited by, liquid phase diffusion of Se evident in microstructures and compositional analyses of individual grains.

The stoichiometry of individual β-Fe₅Se₇ grains at maximum yield within the two-phase field is Fe₁₀₂₋₄ₓ₋₀.₀₁₃Se as determined by EPMA analyses. This stoichiometry for β-Fe₅Se₇ is consistent with the optimum composition of Fe₁₀₂₋₀.₀₀₃₋₀.₀₁³Se [13] obtained via similar synthesis methods and determined using neutron diffraction. An alternative synthesis method, using higher temperatures and longer annealing times, determined the optimum stoichiometry for the tetragonal phase at Fe₁₀₂₋₀.₀₀₃₋₀.₀₁³Se [10] also using neutron diffraction. In all previous studies, the presence of secondary phases such as α-Fe, Fe₂Se₃ or δ-Fe₅Se₇ is documented. In this study, detailed microstructural and compositional analyses of 13 separate syntheses, correlated with phase identification using BSE imaging, show that β-Fe₅Se₇ forms in conjunction with δ-Fe₅Se₇ for 330 °C < Tₘ < 750 °C and 0.89 < x < 1.03 with or without annealing above 400 °C. The microstructures obtained in this work suggest the formation mechanism is via diffusion limited exsolution.

Given the importance of the Fe–Se phase diagram to a fundamental understanding of the superconducting properties of chalcogenides, we suggest that a re-evaluation of physical and chemical characteristics across a broader range of
starting compositions and reaction temperatures may be useful. Key attributes that may benefit from further attention to detail include (i) clarification on the presence/absence of a peritectic transition at 457 °C; (ii) extent of a two-phase field for β-Fe₃Se with α-Fe at higher Fe at %; (iii) relationship of FeSe phases at T_{max} < 330 °C with annealing and (iv) nature of vacancy ordering with β-Fe₃Se stoichiometry.

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