

Electronic Supplementary Information:

Low-Temperature Synthesis of Superconducting Iron Selenide Using a Triphenylphosphine Flux

M. Jewels Fallon, Andrew J. Martinolich, Annalise E. Maughan, Leighanne C. Gallington, James R. Neilson

Reactions were completed with varying mole ratios of FeSe:PPh₃ (1:0.5, 1:1, 1:1.5, and 1:2), reaction temperatures (150, 200, 250, 275, 325, 350, 375, and 400 °C), reaction times (16, 24, 72, 117, and 168 h), and cooling times (water quench, air quench, 30 h, 45 h, 60 h).

Table S1: Phase fraction (mol%) determined through Rietveld analysis of PXRD patterns of products formed from reactions with varying fluxes.

	β -FeSe	α -FeSe	Fe ₃ Se ₄	FeSe ₂	Fe	Se
Triphenylamine	0.9		4.7	21.9	7.8	64.7
Eicosane	7.2	2.5	7.5	82.8		
No flux	46.3	6.1	39.4		8.2	

Phase fractions calculated from *in situ* XRD (Figure S2) do not take into account amorphous phases. Triphenylphosphine is also not included in this analysis as the peaks for this phase are barely observable due to the large X-ray scattering cross-section of iron. Additionally, spots observed in the diffraction pattern before data reduction indicate iron single crystal formation that could impact the phase fractions. Triphenylphosphine selenide is observed in the room temperature PDF indicating that ball milling initiated adduct formation which accounts for the excess iron compared to selenium observed in the diffraction at room temperature.

Laboratory *ex situ* PDF analysis of the reaction 8Fe + Se + PPh₃ (Figures S3, S4) was completed using HighScore Plus to reduce the data and PDFgui to model the data. Each of these PDF

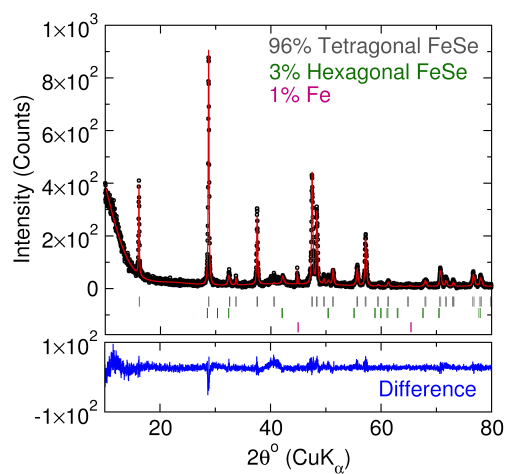


Figure S1: Diffraction pattern of products from the reaction between PPh_3Se and Fe. Rietveld analysis is shown in red and difference curve in blue. The tick marks indicate peak locations for $\beta\text{-FeSe}$ (grey), $\alpha\text{-FeSe}$ (green), and Fe (pink) and the phase fraction (mol%) is shown in the upper righthand corner.

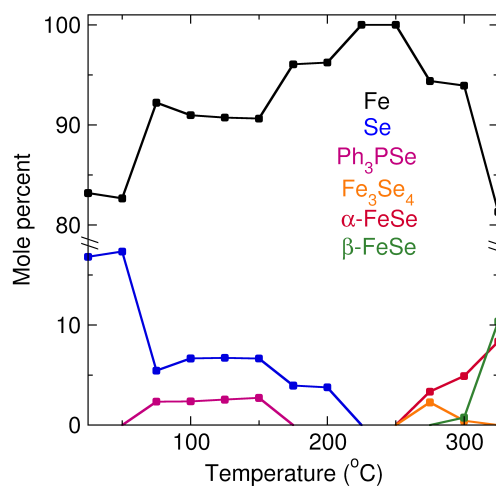


Figure S2: Phase fraction (mol%) of each phase determined from Rietveld analysis of PXRD data collected *in situ* during the iron selenide reaction.

Table S2: Inorganic reaction products across the ternary Fe-Se-PPh₃ phase space. Phase fraction (mol%) are written in parentheses.

Ratio Fe:Se:PPh ₃	Product 1	Product 2	Product 3	Product 4	Product 5	Product 6
3:1:6	β-FeSe (88)	Fe (12)				
1:3:6	β-FeSe (95)	α-FeSe (5)				
1:1:8	β-FeSe (98)	Fe (2)				
8:1:1	β-FeSe (61)	Fe (39)				
6:3:1	β-FeSe (93)	Fe (7)				
6:1:3	β-FeSe (71)	Fe (29)				
1:8:1	Se (93)	β-FeSe (4)	FeSe ₂ (3)			
3:6:1	Se (48)	FeSe ₂ (27)	β-FeSe (16)	Fe ₃ Se ₄ (7)	α-FeSe (2)	
1:6:3	Se (57)	FeSe ₂ (14)	Fe (18)	β-FeSe (6)	Fe ₃ Se ₄ (4)	α-FeSe (1)
4:2:4	β-FeSe (93)	Fe (7)				
2:4:4	β-FeSe (84)	α-FeSe (16)				
4:4:2	β-FeSe (93)	α-FeSe (7)				

data sets were modeled with two iron phases along with the other phases present. The crystalline iron phase was modeled through refining lattice parameters, thermal parameters, correlated motion parameters, and the scale factor. The amorphous iron phase was modeled by duplicating the crystalline iron phase but with a spherical particle size cut-off which refined to 7 Å.

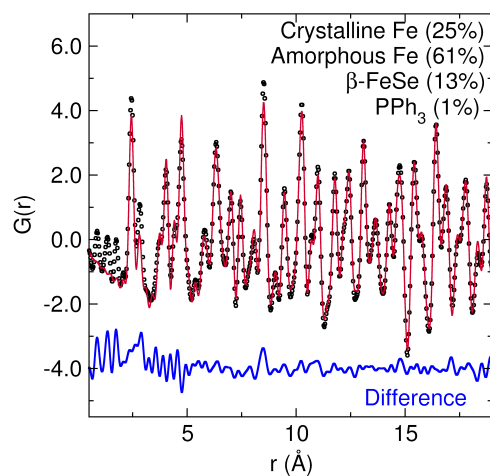


Figure S3: *Ex situ* PDF analysis of of 8Fe + Se + PPh₃ reaction product. The phase fractions (mol%) of the refined phases are included in the top right corner. The data are shown as black circles, the fit is the red line, and the difference is the blue line.

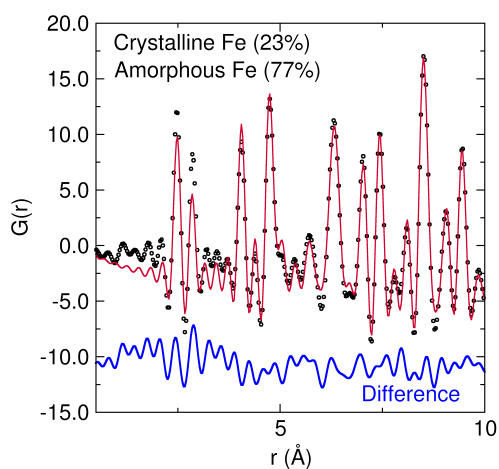


Figure S4: *Ex situ* PDF analysis of the iron starting material. The phase fractions (mol%) of the refined phases are included in the top left corner. The data are shown as black circles, the fit is the red line, and the difference is the blue line.

Table S3: Formation energies accessed from the Materials Project (Date: 5/16/2019).²

Compound	Formation energy (eV/atom)	Materials project ID
Fe	0	mp-13
FeSe	-0.276	mp-20311
FeSe ₂	-0.348	mp-760
Se	0	mp-570481