The reactions between iron and selenium

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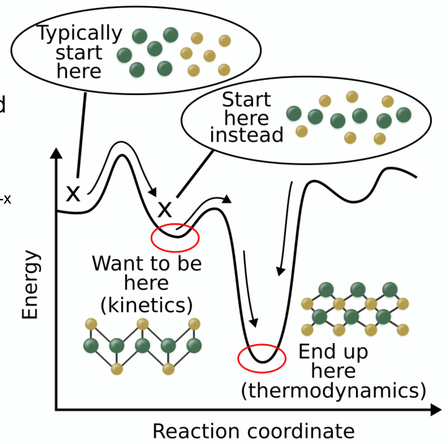
Introduction

Purpose:

- The recent discovery of high temperature superconductivity ($T_c \approx 80K$) in β-FeSe crystals has sparked a global research effort in iron selenide materials.[1]
- A vast diversity of synthetic routes have emerged in attempt to isolate the superconducting β-FeSe structure, but few have explored the fundamental atomic interactions between iron (Fe) and selenium (Se) leading to these structures.

Problem:

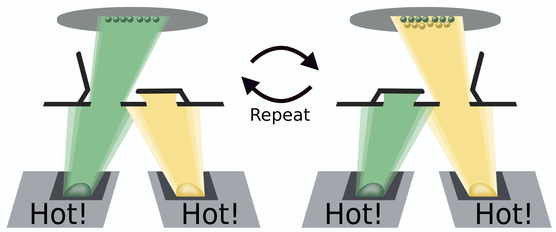
- Formation of a specific crystal structure is complicated by both thermodynamics and kinetics.
- The thermodynamic interactions of Fe and Se are well known, but long atomic diffusion distances have limited our understanding of kinetically stable Fe_xSe_{1-x} materials.



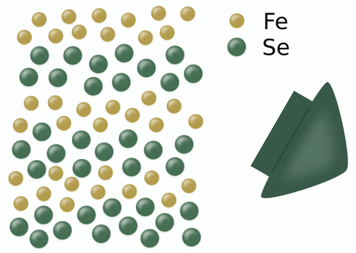
Research Focus:

- Elucidate kinetic mechanisms in the reactions between Fe and Se in the absence of diffusion limitations by preparing Fe_xSe_{1-x} precursors to mimic known structures of FeSe with sub-nanometer resolution.

Methods: Synthesis and Characterization

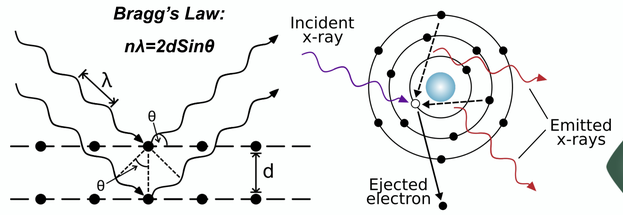


Sub-nano layers of Fe and Se are sequentially deposited onto Si wafers in a high vacuum chamber. Layer thicknesses and composition are tunable via shutter cycles.

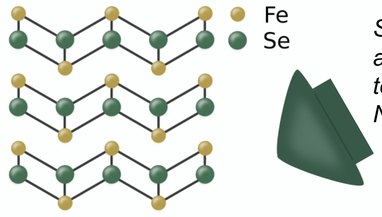


Compositionally modulated precursors are designed to mimic targeted structures.

Samples are heated at temperatures up to 450°C in an inert N_2 atmosphere.



X-ray diffraction (left) and x-ray fluorescence[2] (right) provide structural and compositional details such as lattice parameters and atomic percent of Fe.

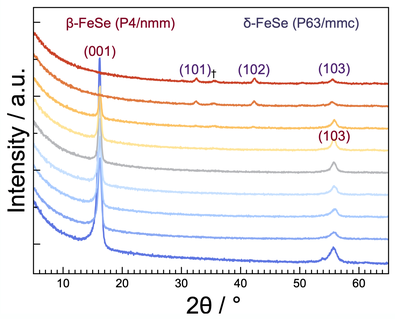


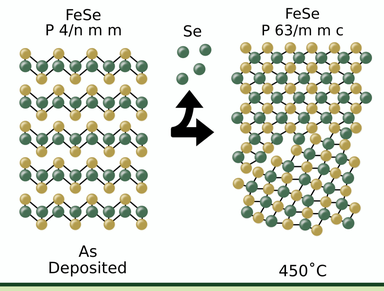
Precursors rearrange into energetically favored and kinetically accessible structures.

Results

FeSe ~ 1:1 ratio:

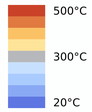
- The crystallization of FeSe phases is found to coincide with those predicted from thermodynamic Fe:Se phase diagrams.
- Fe reacts with Se to form β-FeSe as soon as they come into contact.
- β-FeSe crystals form with crystallographic alignment to the substrate.
- Annealing at higher temperatures results in formation of δ-FeSe.

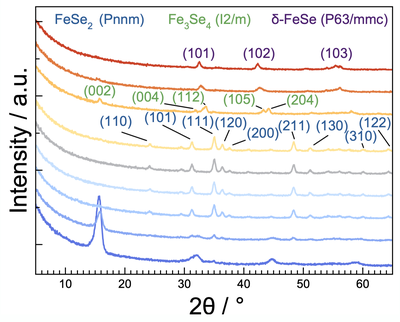


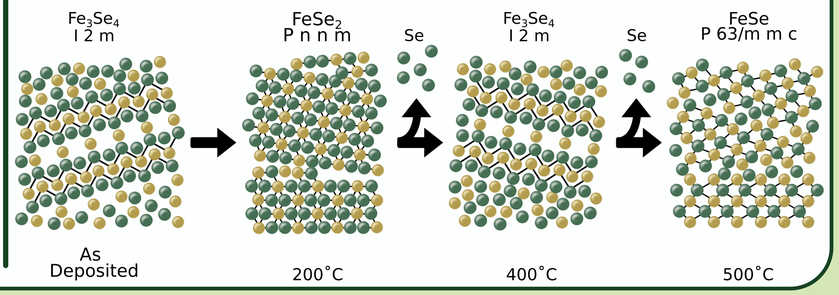


$FeSe_2$ ~ 1:2 ratio:

- Kinetic intermediates are formed before Fe and Se react to form $FeSe_2$.
- By 200°C, the system falls under thermodynamic control.
- Higher temperatures and loss of Se causes system to shift towards thermodynamic Fe rich phases Fe_3Se_4 and eventually δ-FeSe at 500°C.







Conclusions

Thermodynamic vs kinetic control:

- Even in the absence of diffusion barriers, thermodynamics appear to dominate the reaction mechanisms between Fe and Se.
- These findings may hold significant consequences for the development of future FeSe-based materials, as the low reaction barriers to form the thermodynamic products may impede efforts to kinetically trap metastable FeSe materials.
- Fortunately, the thermodynamic stability of the two dimensional (2D) superconductor β-FeSe phase may be exploitable in the synthesis of heterostructures interweaving FeSe and other 2D materials.

Future work:

- Explore the interactions between FeSe and other 2D materials by preparing heterostructure precursors using the method described above.
- Elucidate the structure and composition of the kinetically stable $FeSe_2$ phase observed on deposition.

Acknowledgements

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References

[1]Q.-Y. Wang et al. *Chin. Phys. Lett.* **2012,** *29,* 037402

[2]Hamann, D.; Bardgett, D.; Cordova, D. L.; Maynard, L. A.; Hadland, E. C.; Lygo, A. C.; Wood, S. R.; Esters, M.; Johnson, D. C. *Chem. Mater.* **2018**, *30*(18), 6209-6216.

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