Synthesis and Characterisation of the New Strontium Silicate Compound $Sr_2Si_3O_8$

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Outline

- Aims of Project
  - •Synthesis Procedures
  - •$Sr_2Si_3O_8$ – Structure
  - •Optimisation
  - •Dopants
- Prospective

The CERAM Team

Aims

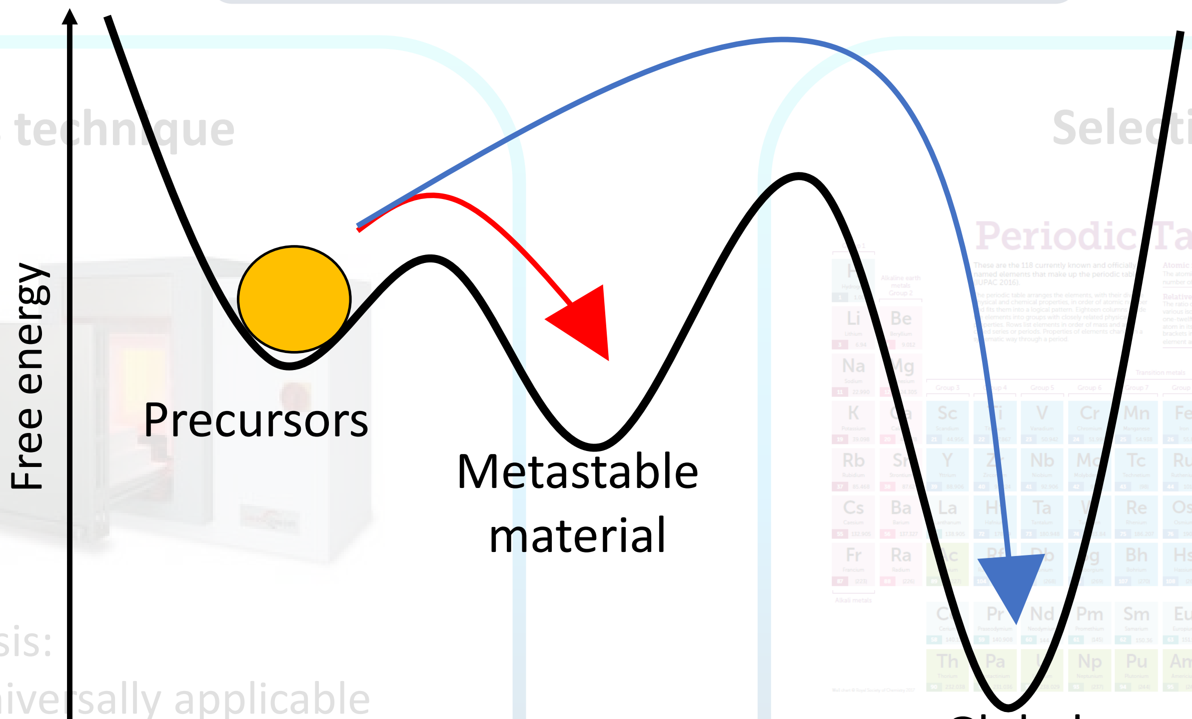
A synthesis-driven inorganic materials discovery project, that uses innovative synthesis approaches to isolate new metastable metal oxides with the potential to support functional properties

Two big factors in materials discovery:

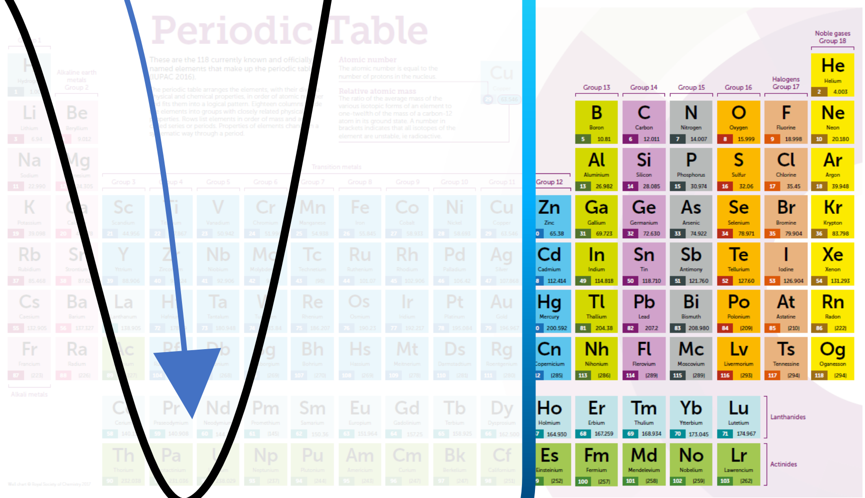
Synthesis technique

Solid-state synthesis:
- Advantage: Universally applicable
- Disadvantage: doesn't favour metastable phases

Metastable phases:

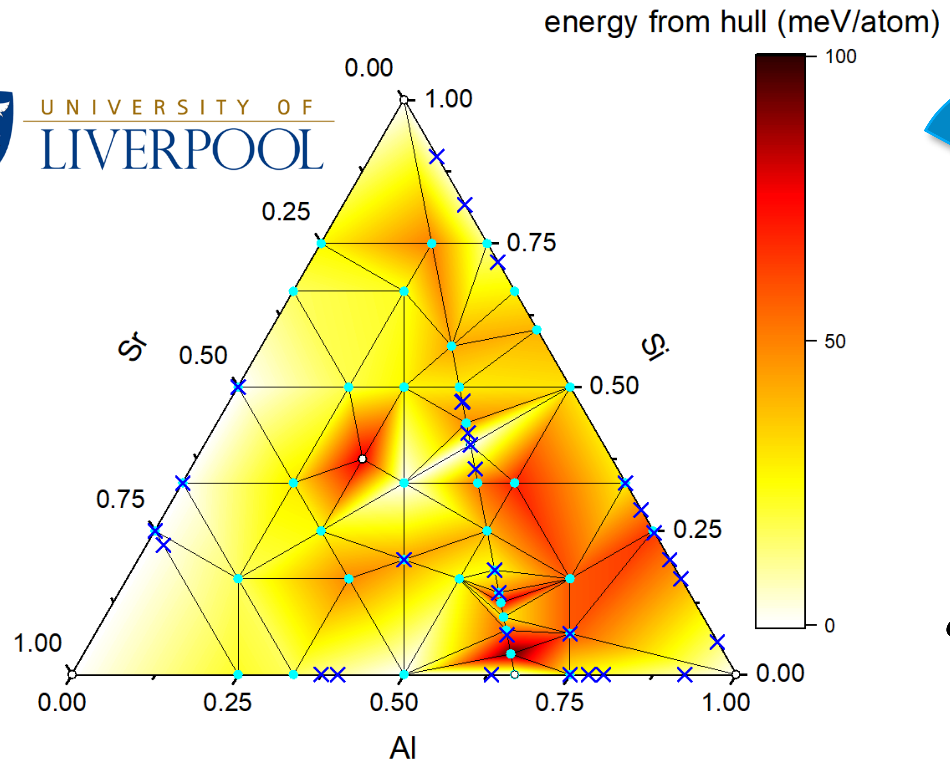


Selection of targets



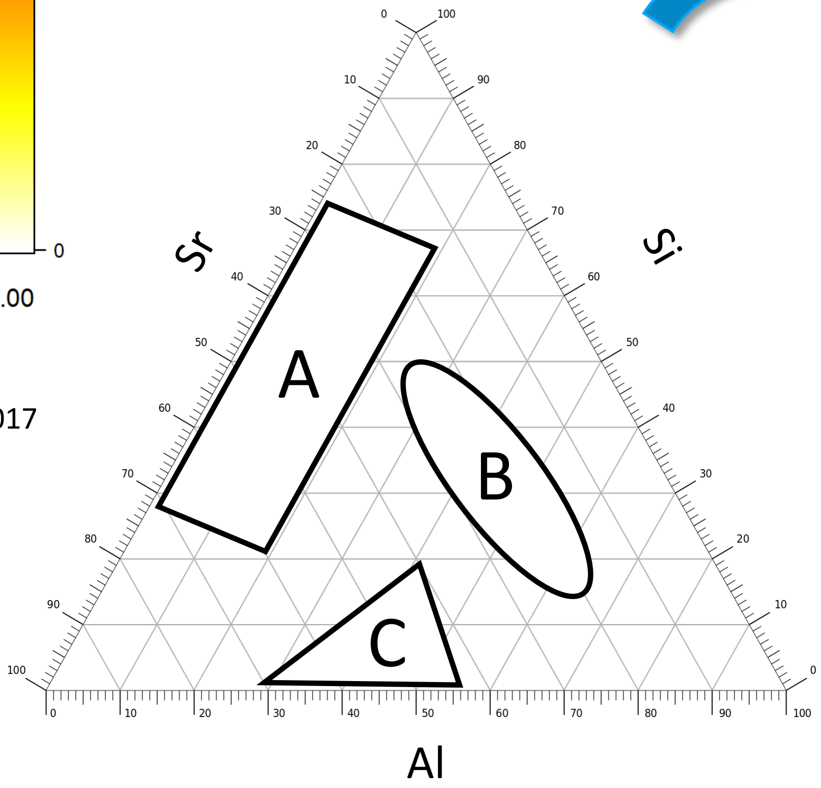
What compositions will form desirable phases?

Computationally Guided



C. Collins, M. S. Dyer, et al *Nature* **546**, 280–284, 2017

Exploration zones



Synthesis trials

Synthesis Techniques

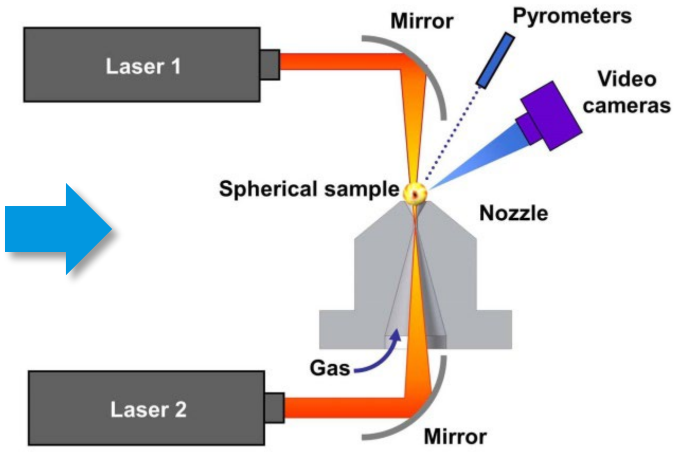
Solid State Reaction

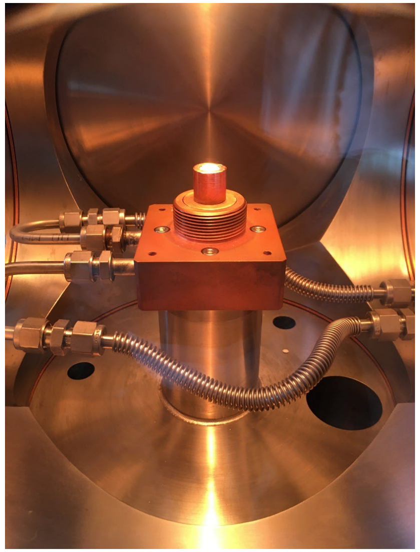
Precursors

+

Sintering

Aerodynamic Levitation (ADL)





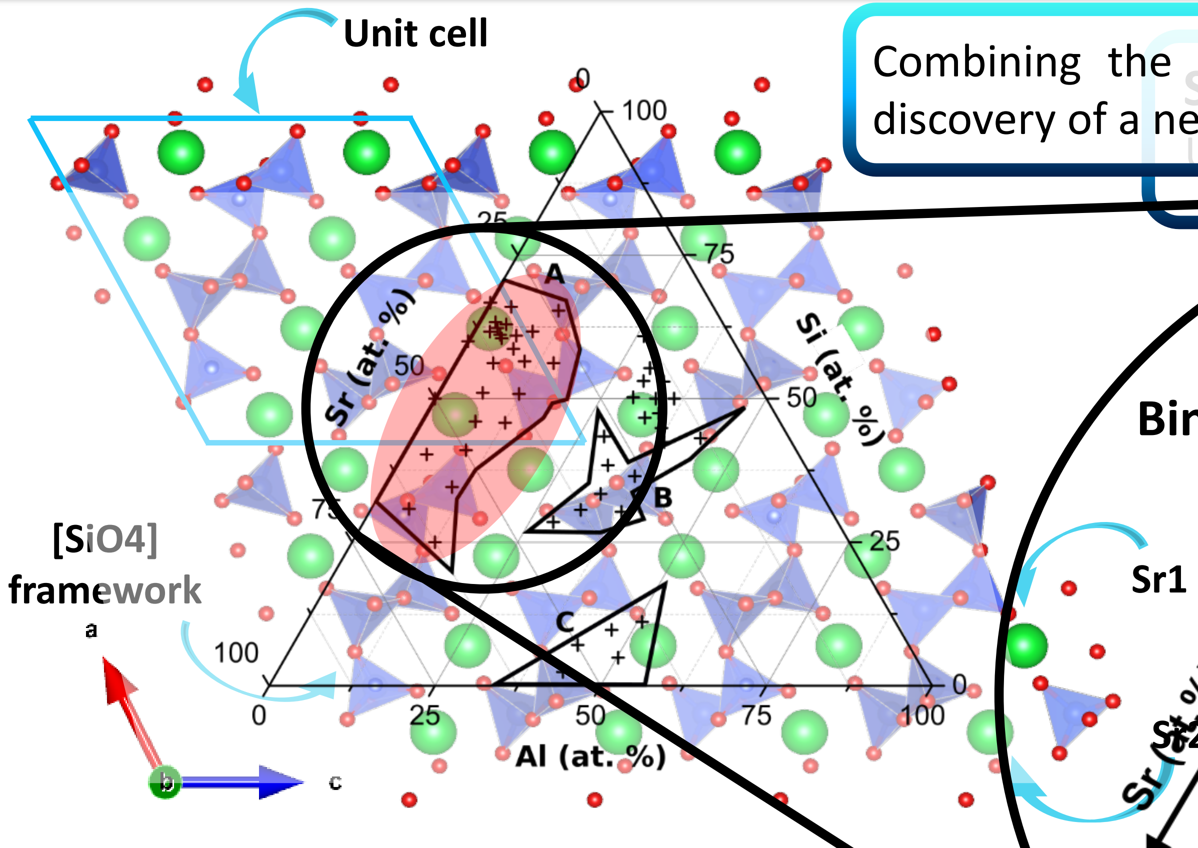
$Sr_2Si_3O_8$ – Structure

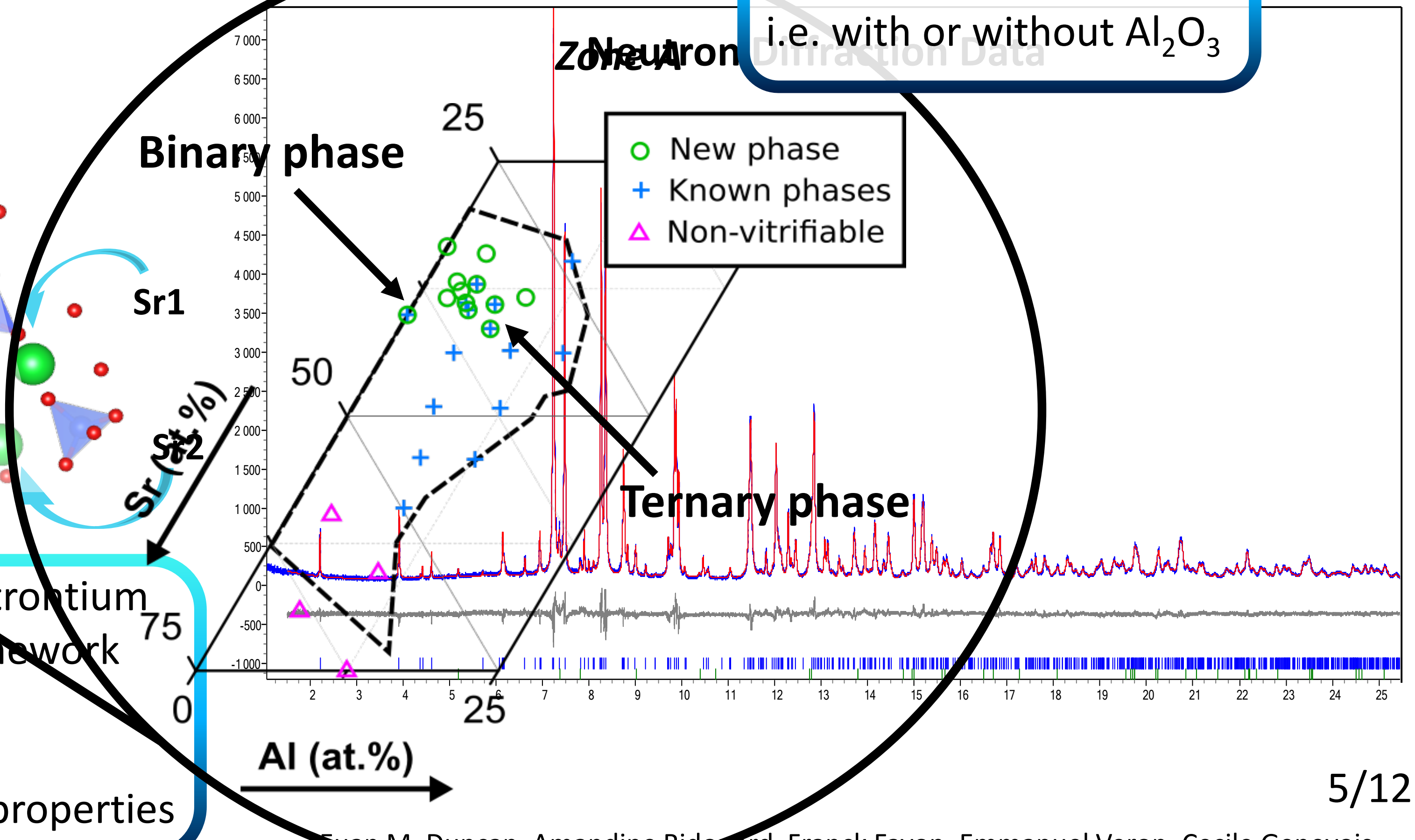
Combining the techniques led to the discovery of a new phase:

$Sr_2Si_3O_8$ Monoclinic - $P2_1/c$

Unit cell - solved ab initio by simulated annealing

Results suggested either a ternary or binary phase i.e. with or without Al_2O_3





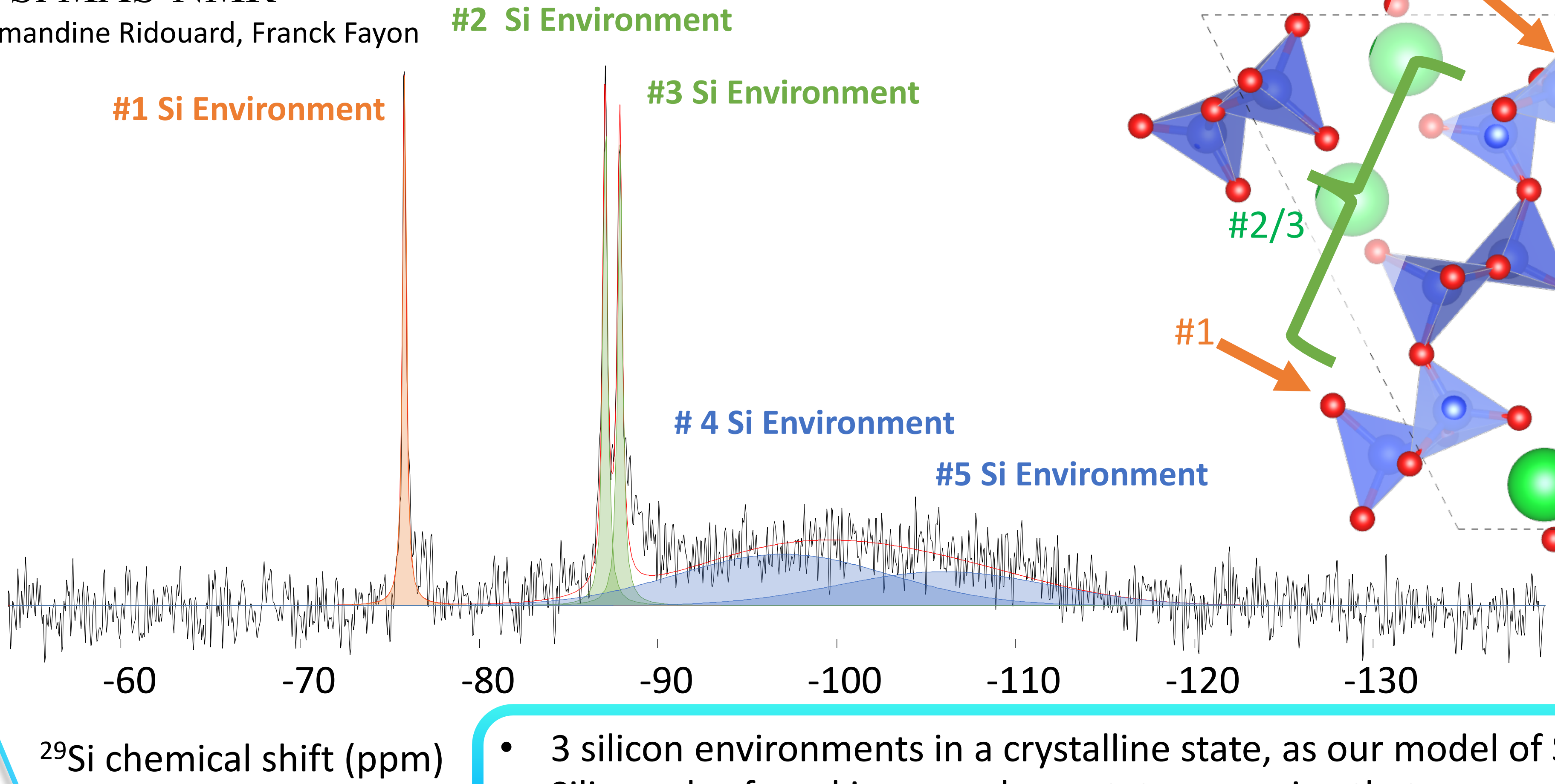
- First ambient-pressure example of a strontium silicate with a polymerised [SiO4] framework
- Potential for mechanoluminescent or luminescent properties
- Synthesis must be improved to study properties

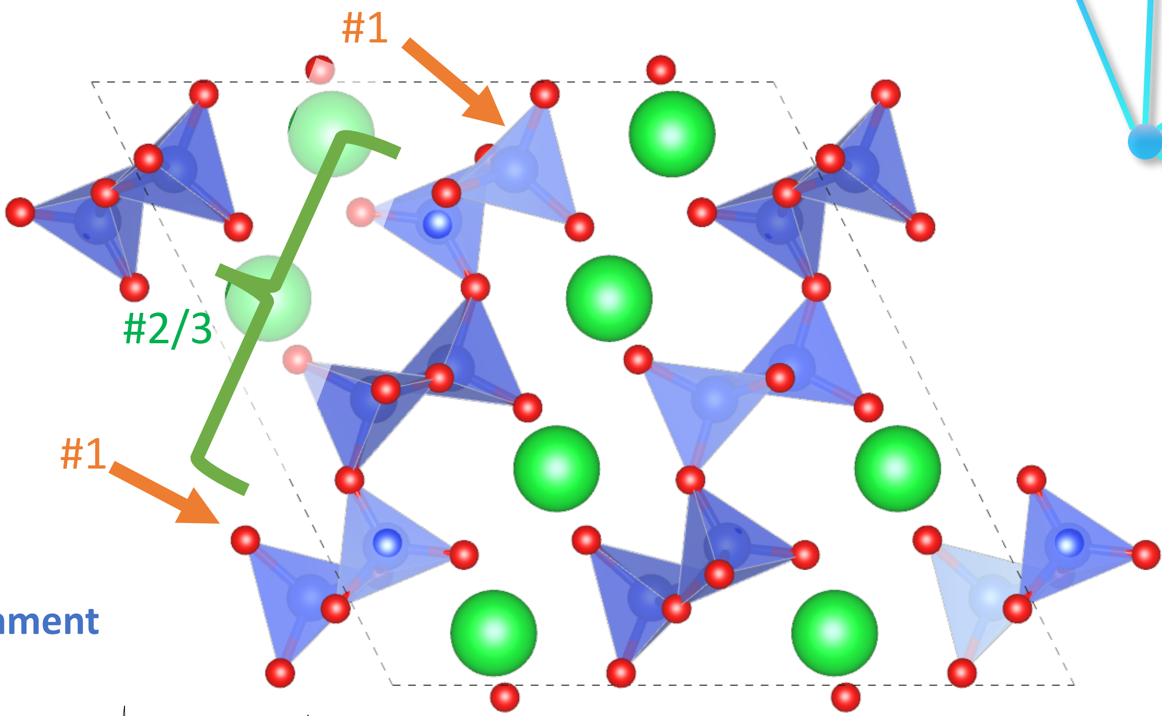
Euan M. Duncan, Amandine Ridouard, Franck Fayon, Emmanuel Veron, Cecile Genevois, Mathieu Allix, Christopher M. Collins, Michael J. Pitcher, *Chem. Commun.*, 2023, 59, 10544

NMR

^{29}Si MAS-NMR

Amandine Ridouard, Franck Fayon

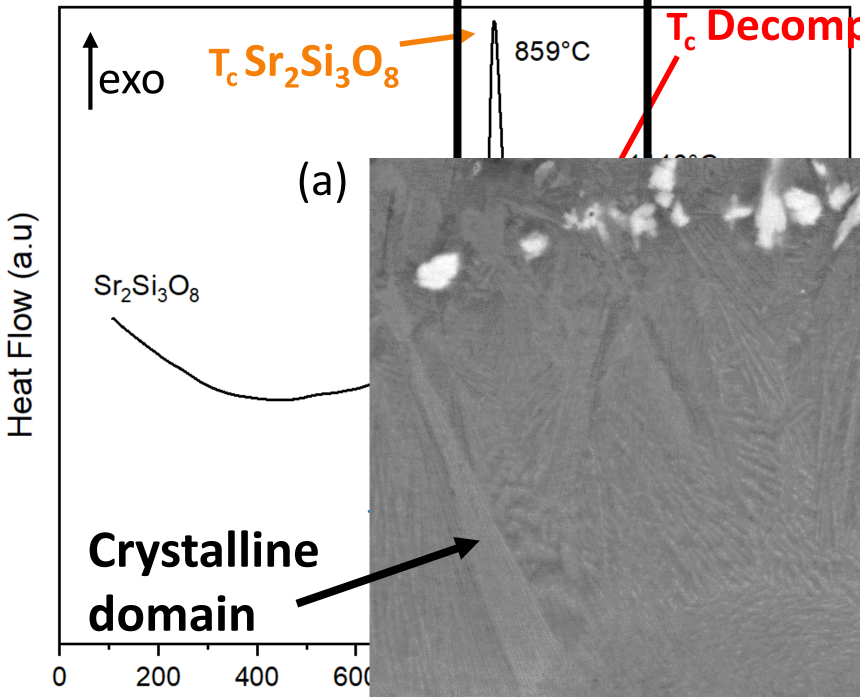




- 3 silicon environments in a crystalline state, as our model of $Sr_2Si_3O_8$ predicted
- Silicon also found in amorphous states meaning that we aren't synthesising it phase pure
- Size of the amorphous bumps suggests a non-negligible glass content

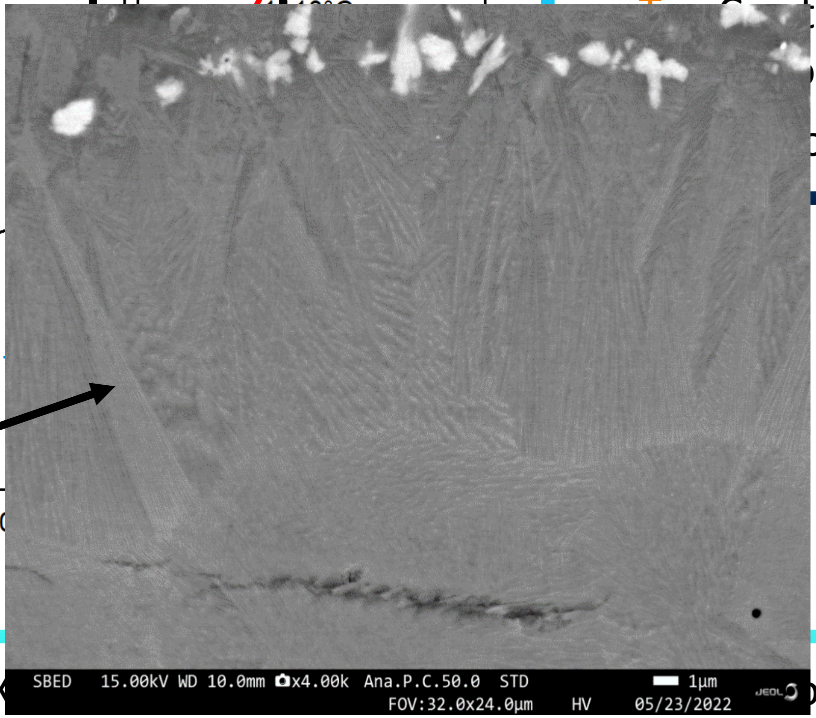
Optimisation

Differential Scanning Calorimetry (DSC)

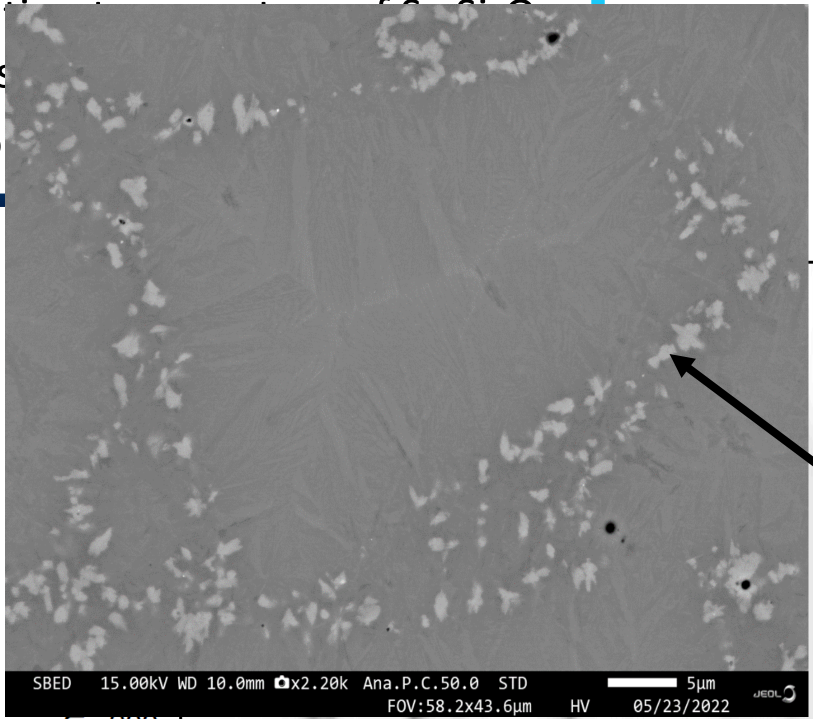


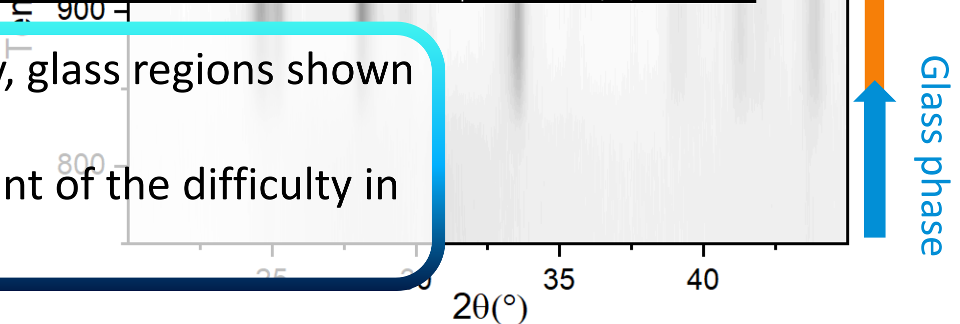
SEM images of $Sr_2Si_3O_8$ at (a) 1µm (b) 5µm

(a)



(b)



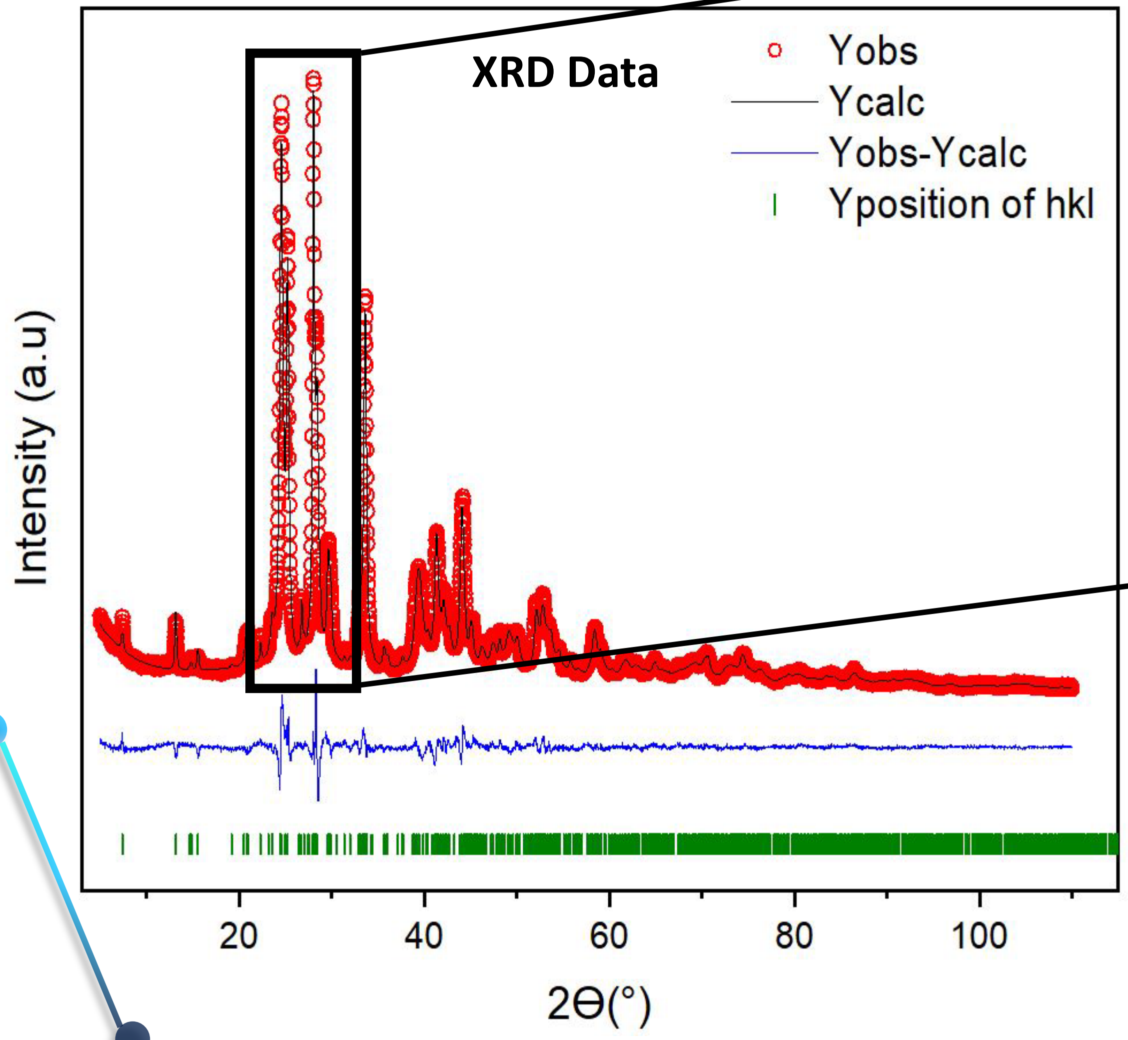


VTX... on
- Desired phase forms between 850 – 1050°C
- In good agreement with the DSC result
- Try crystallisation experiments within this temperature range

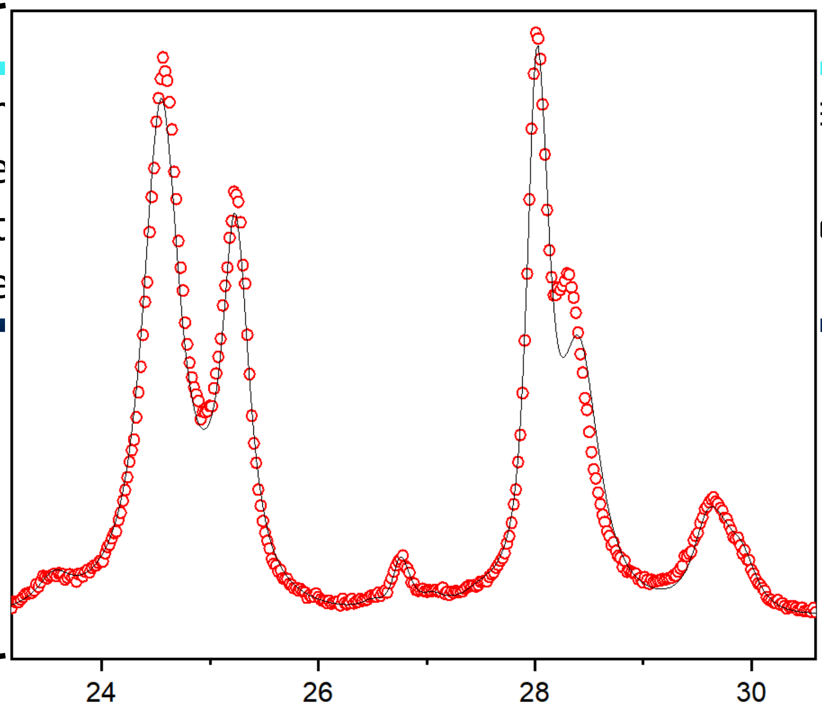
Crystal regions shown in dark grey, glass regions shown in light grey

Small crystalline domains – first hint of the difficulty in synthesising this phase pure

Optimisation



- Best syr … and a heat treatme…
- This dat … ce group
- Howeve…

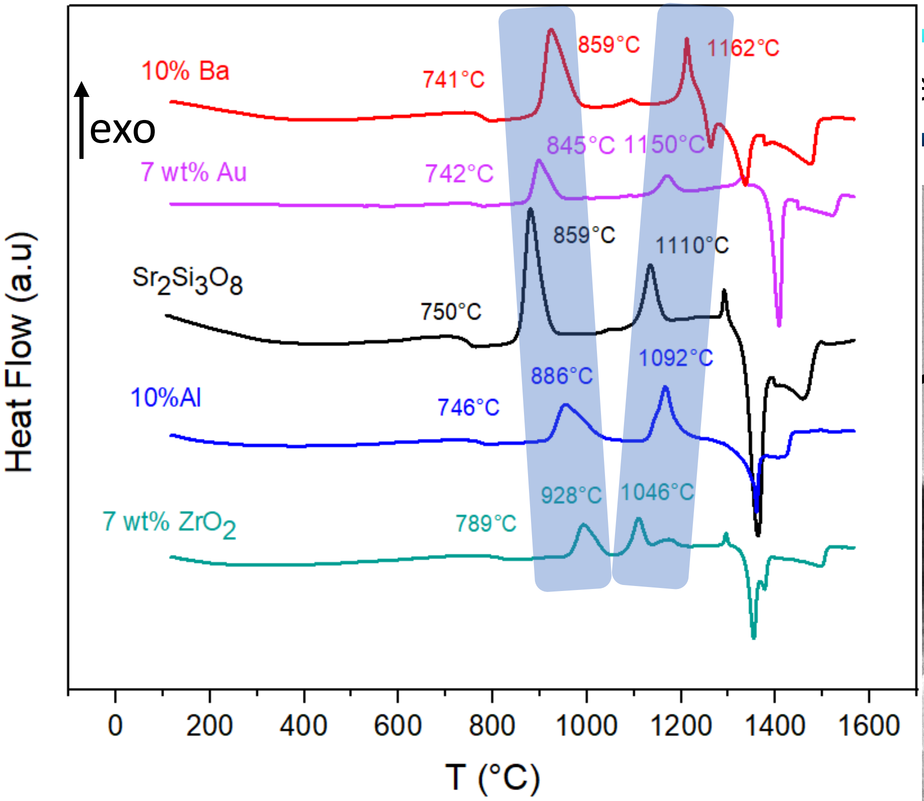


- Unable to fit the shoulder on the peak at 28°
- Crystallisation achieved in excess of 85%
- Still a remaining glassy phase
- Trade off between crystalline quality and crystalline quantity

What is happening microstructurally to explain this?

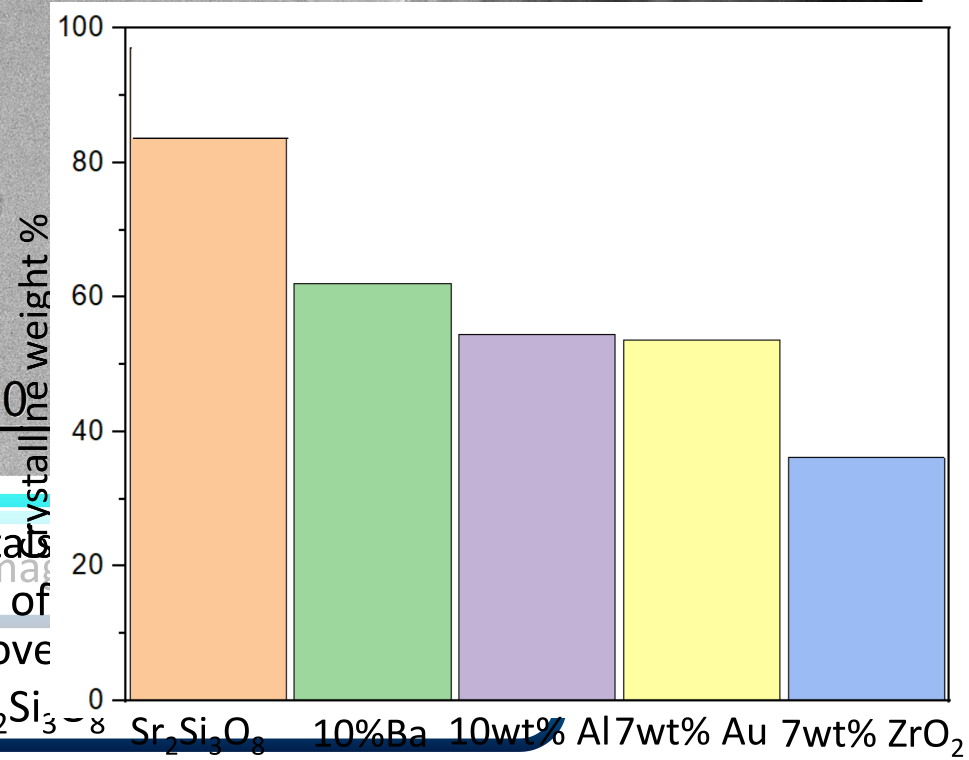
Nucleating agents / Dopants

- Aim to increase the $T_c - T_c$ gap to stabilise the $Sr_2Si_3O_8$ phase
- Barium and gold increased the gap but lowered the overall crystal phase content
- Zirconia and aluminium decreased the gap and decreased the overall crystalline weight %

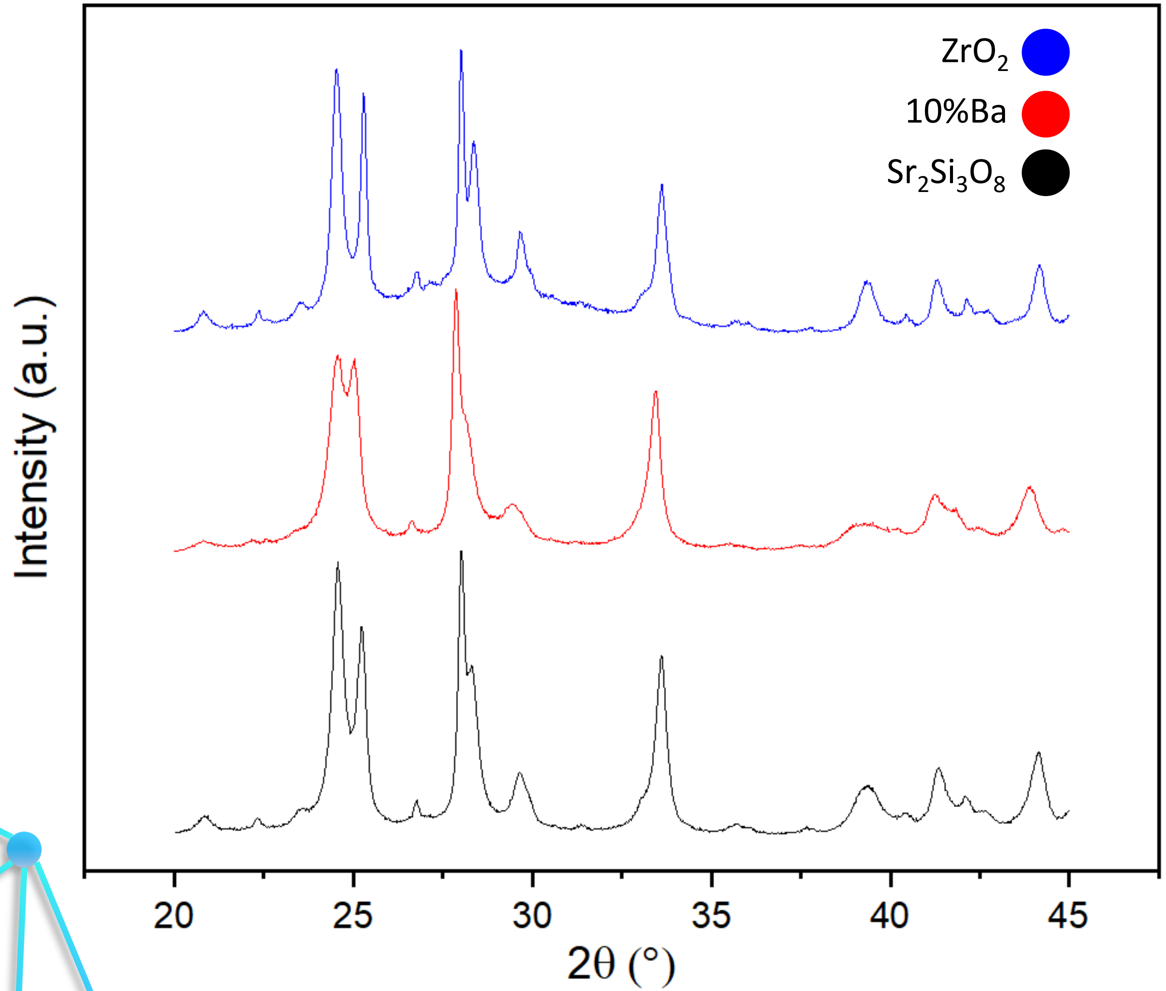


- The original $Sr_2Si_3O_8$ sample gives the highest crystalline weight %
- Very hard to make the sample phase pure

- Cloudiness suggests glass either above small/thin crystalline domains of $Sr_2Si_3O_8$

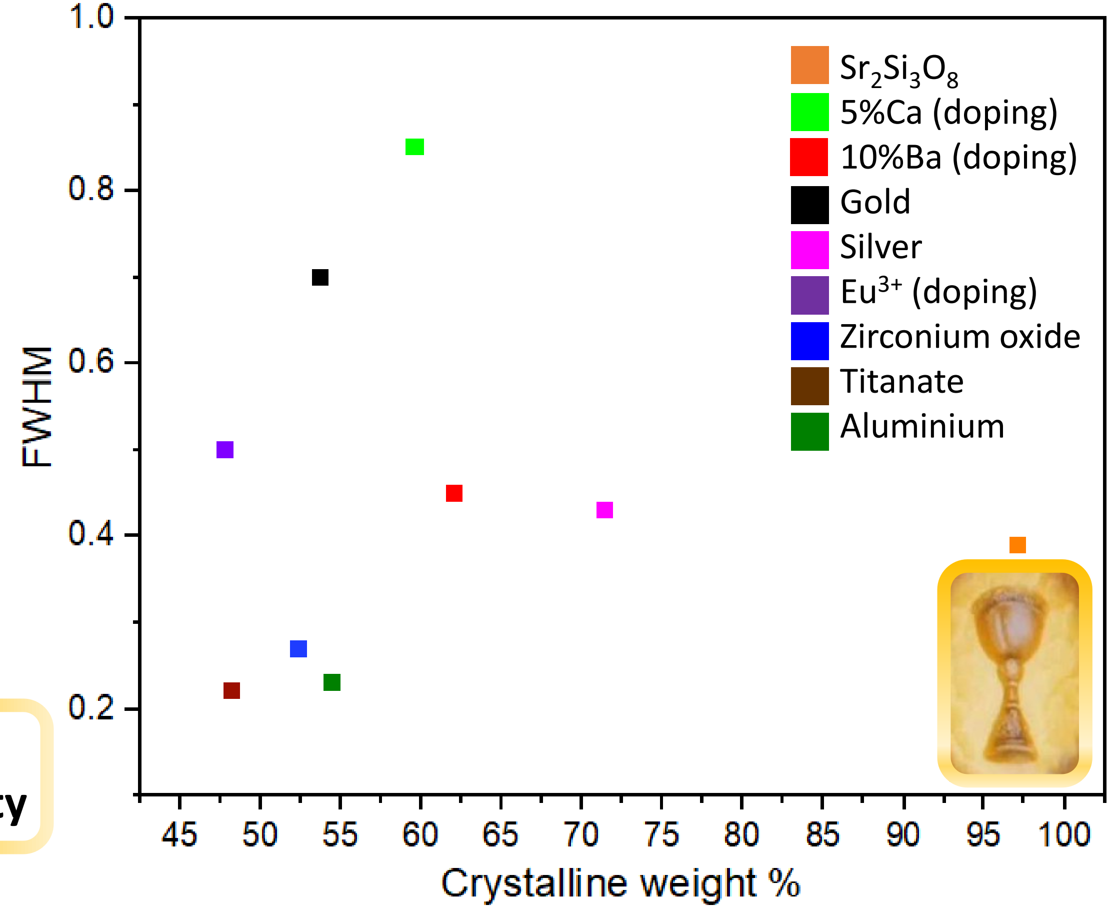


Nucleating agents / Dopants



3 families of behaviour can be seen:

- ‘Normal’ $Sr_2Si_3O_8$ pattern
- Crystallinity and peak sharpness is decreased
- Crystallinity decreased but peak sharpness increased



Aiming for holy grail zone
high crystallinity and high crystalline quality

Prospective

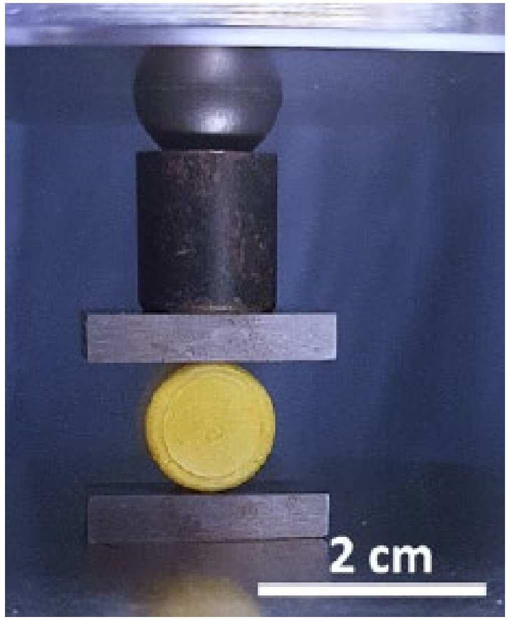
Trying other non-equilibrium synthesis techniques which may offer a route to metastable phases & also avoid the glass stage

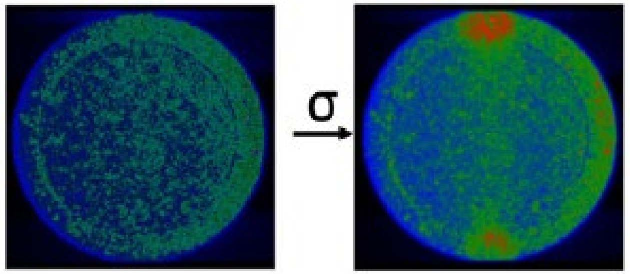
Spray Dryer

High Energy Ball Mill

Uniform crystallisation of $Ba_2Si_3O_8$ was achieved through the incorporation of nitrogen into the glass
This phase also exhibits mechanoluminescent properties

Alexis Duval, Patrick Houizot, Xavier Rocquefelte, Tanguy Rouxel Appl. Phys. Lett. 123, 011905 (2023)





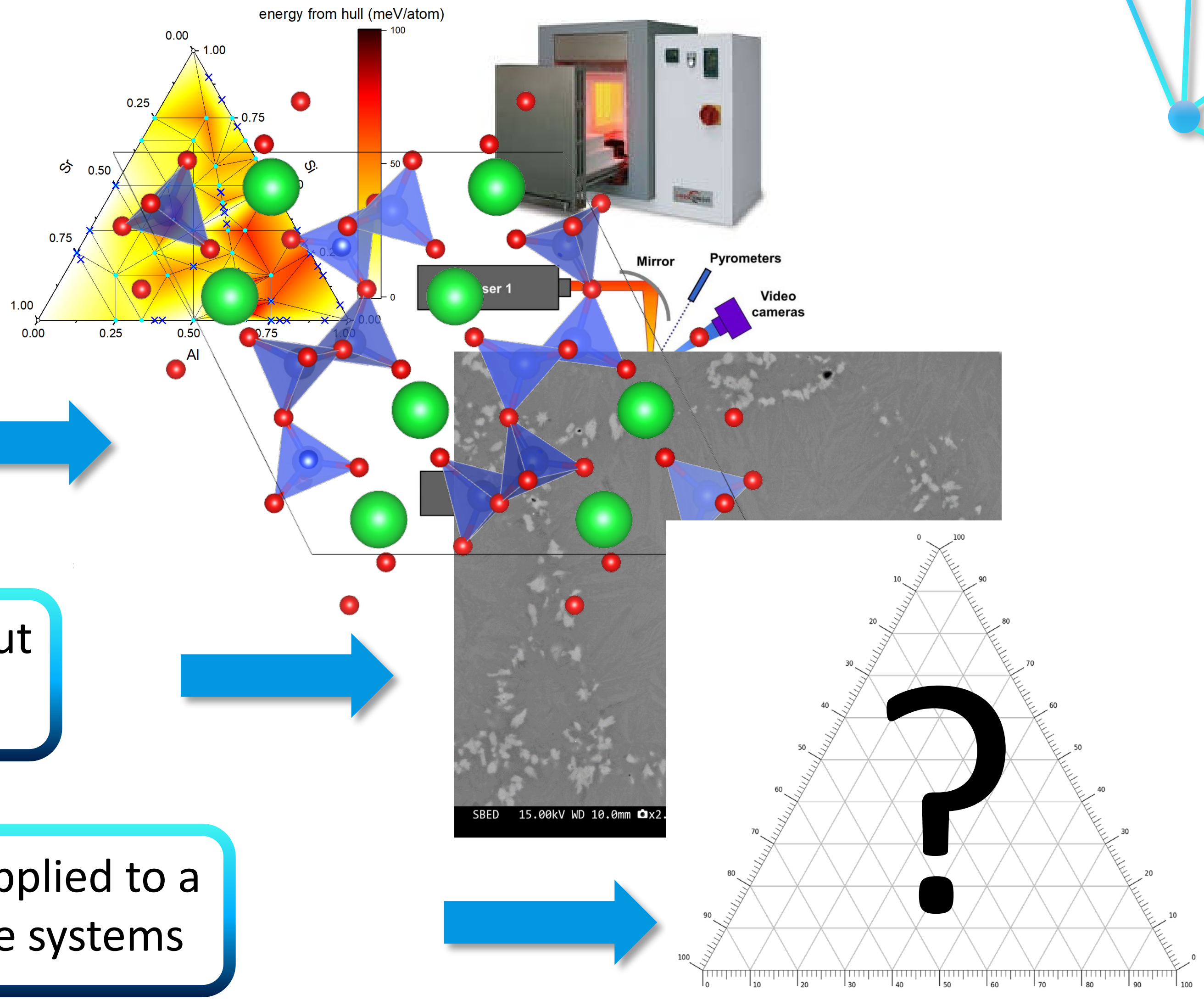
Conclusion

By using two innovative synthesis techniques
+
Computational guidance

Managed to find the new $Sr_2Si_3O_8$ phase

Hard to make this phase without a glassy phase present

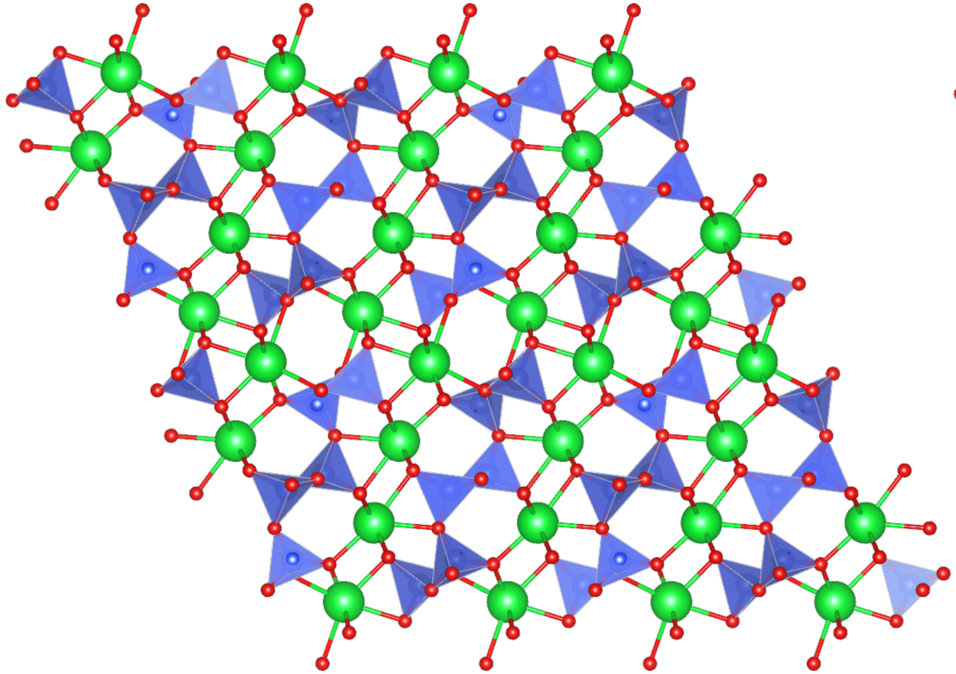
Technique can be applied to a wide range of oxide systems



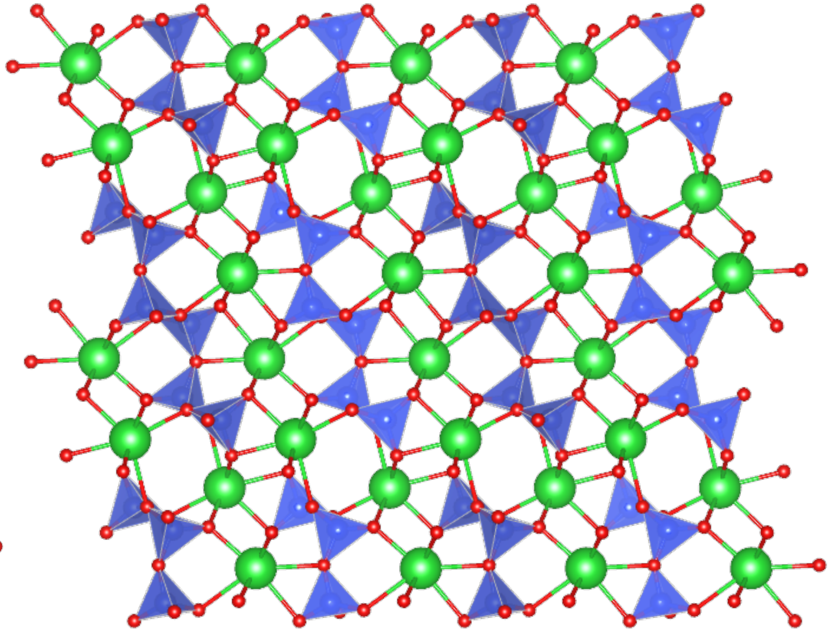
Thank You For Your Attention!

Any Questions?

$Sr_2Si_3O_8$



$Ba_2Si_3O_8$

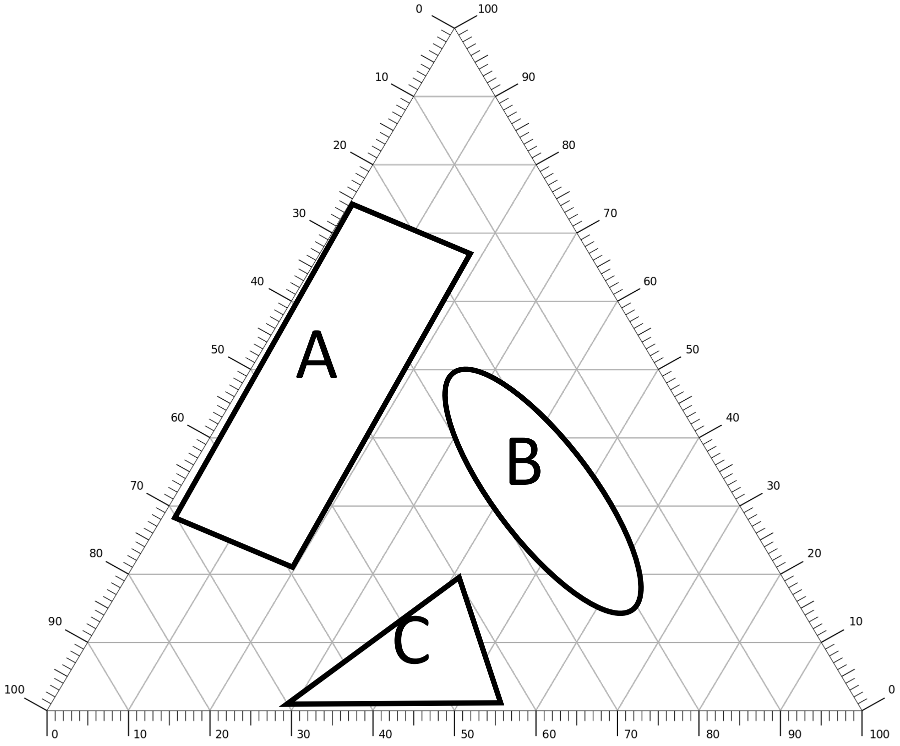


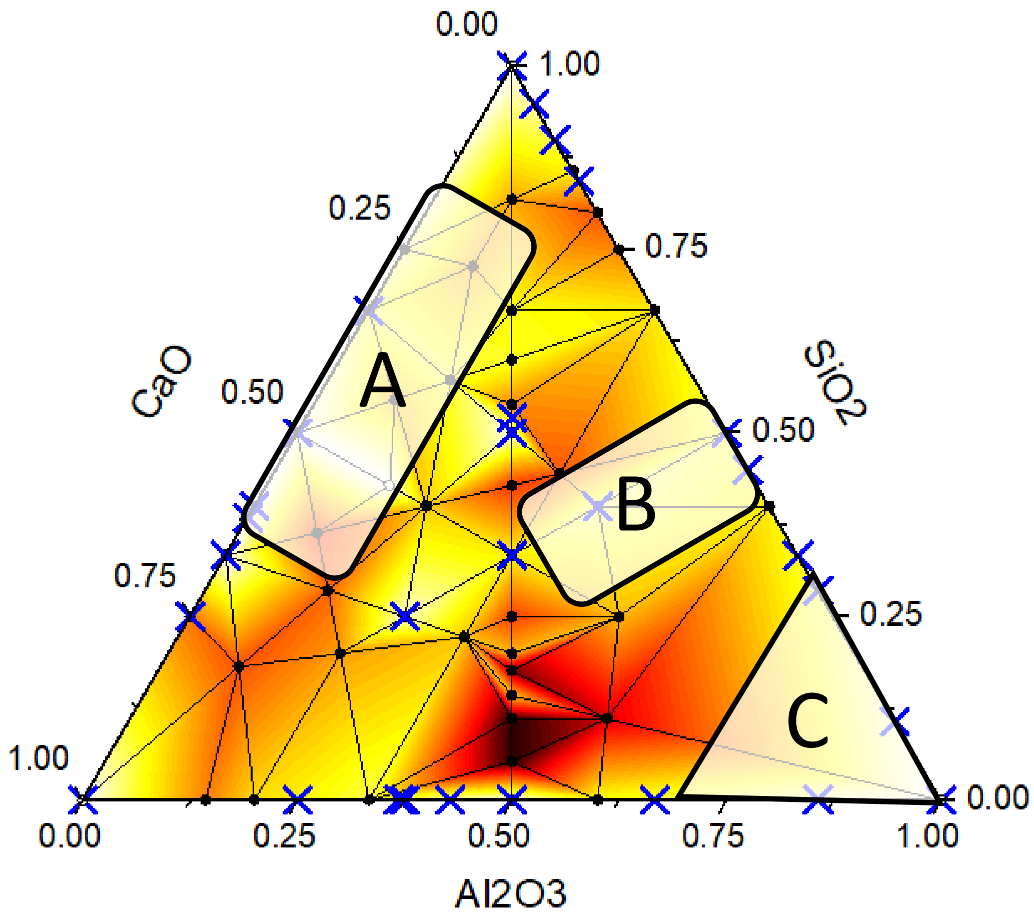
- SiO_4 Zwier ribbons have different topologies
- $Sr_2Si_3O_8$ is a one-dimensional structure whose main feature is a [Si6O16]8_ ribbon, formed by three zweier chains that are linked into 6-membered rings of tetrahedra in ududud orientation.

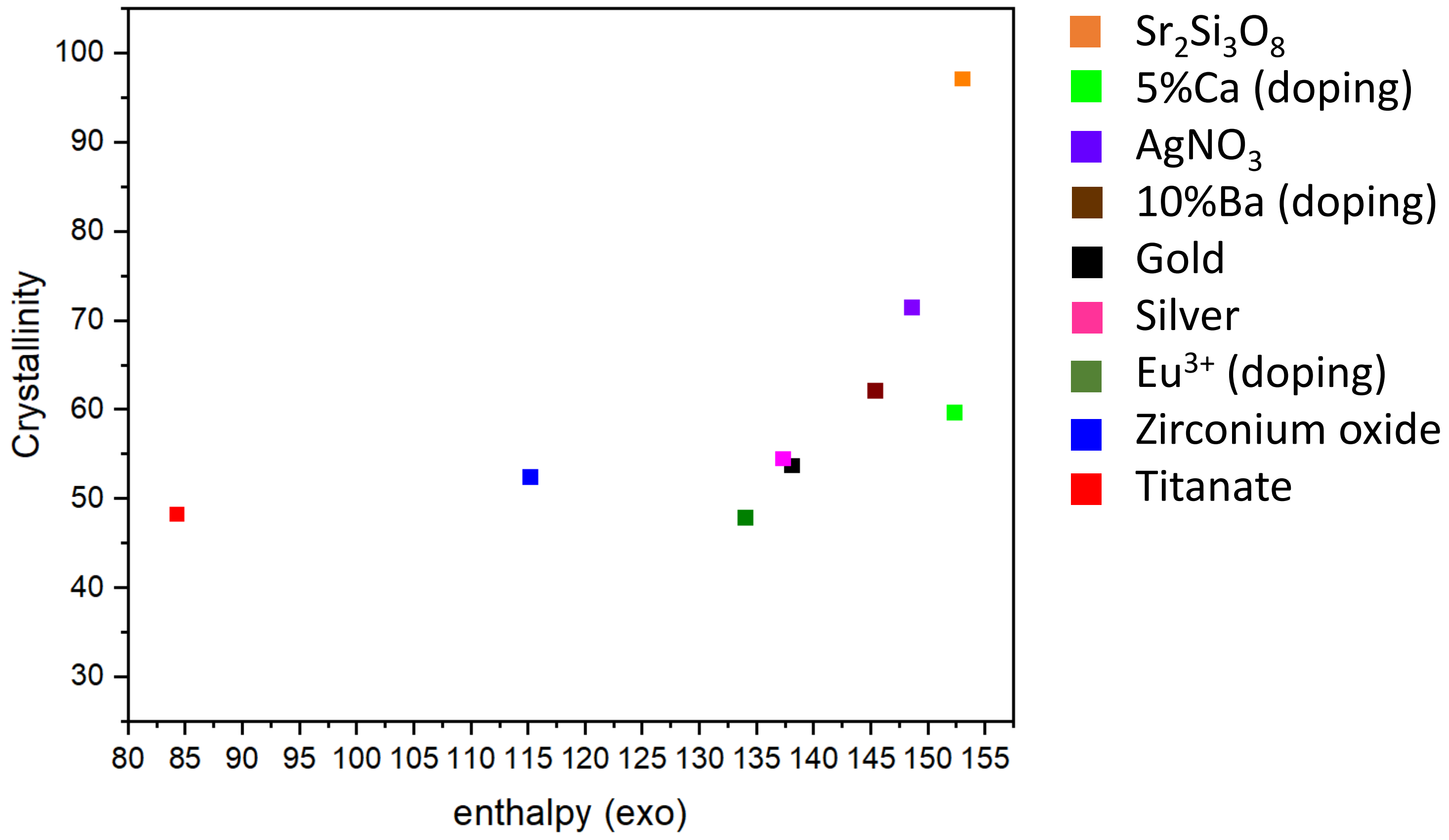
Prospective

Found a new phase inbetween two known solid state solutions
With luminescent properties

Try the same procedure for other ternary diagrams
e.g. CaO-SiO_2-Al_2O_3 phase diagram







Crystallinity
100
90
80
70
60
50
40
30
80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155
enthalpy (exo)
$Sr_2Si_3O_8$
5%Ca (doping)
$AgNO_3$
10%Ba (doping)
Gold
Silver
Eu^{3+} (doping)
Zirconium oxide
Titanate