



# Growth pressure effects and physical properties of high $T_c$ iron-based superconductors

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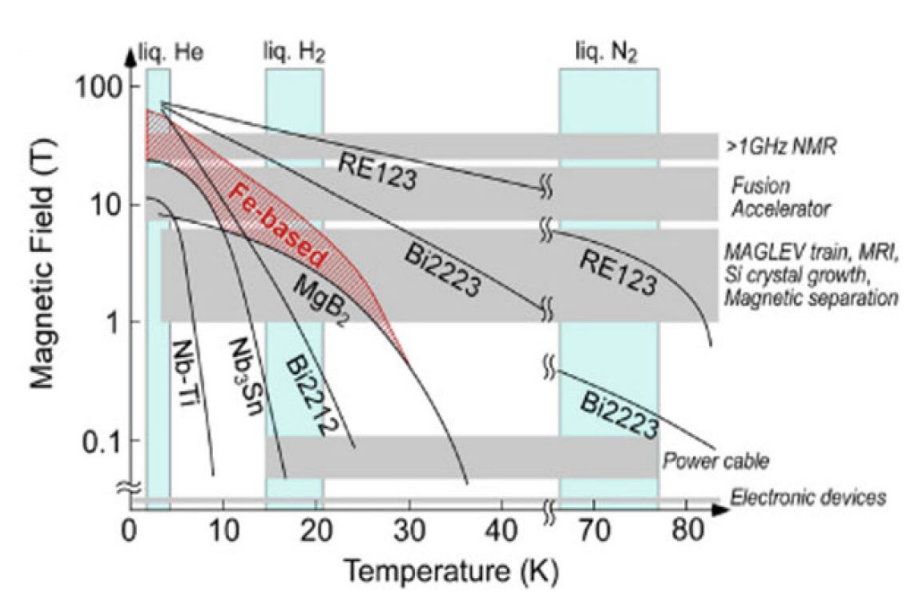
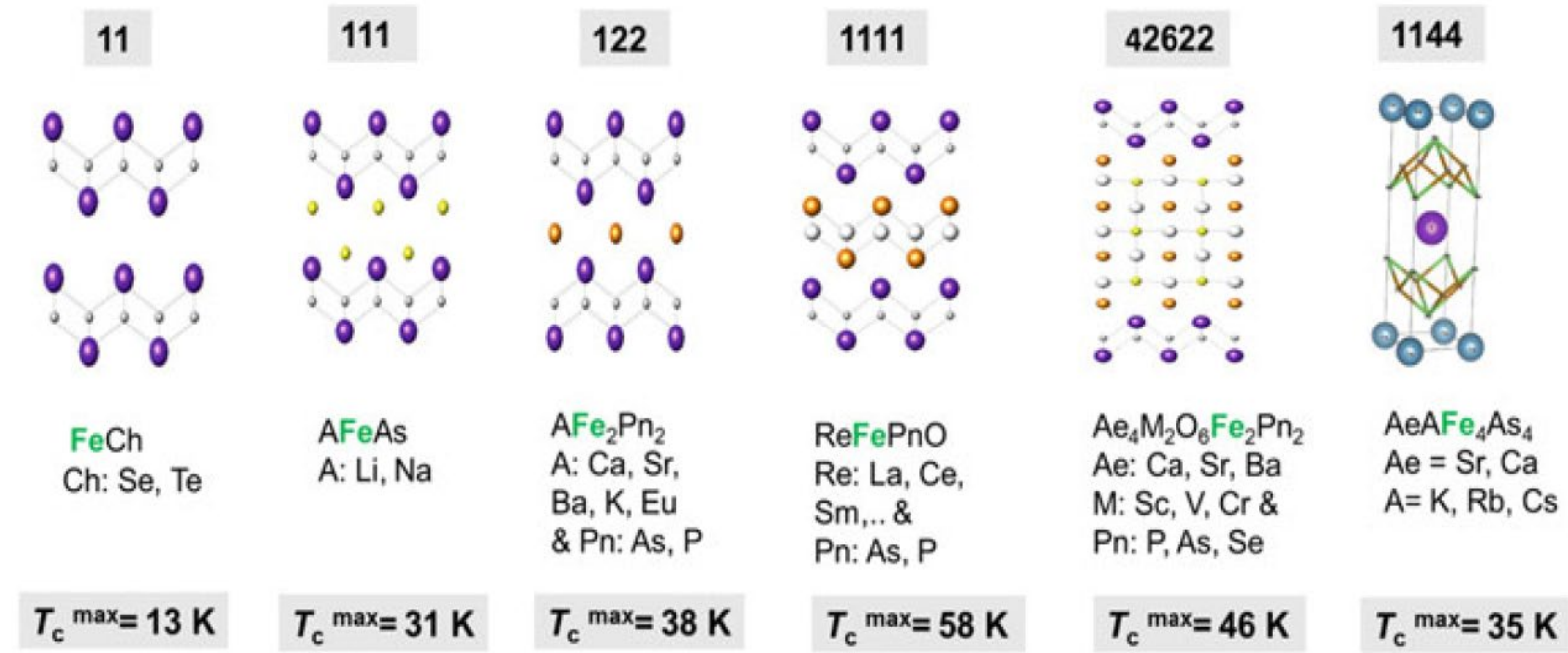


**Dr. Tomasz Cetner (Technician)**



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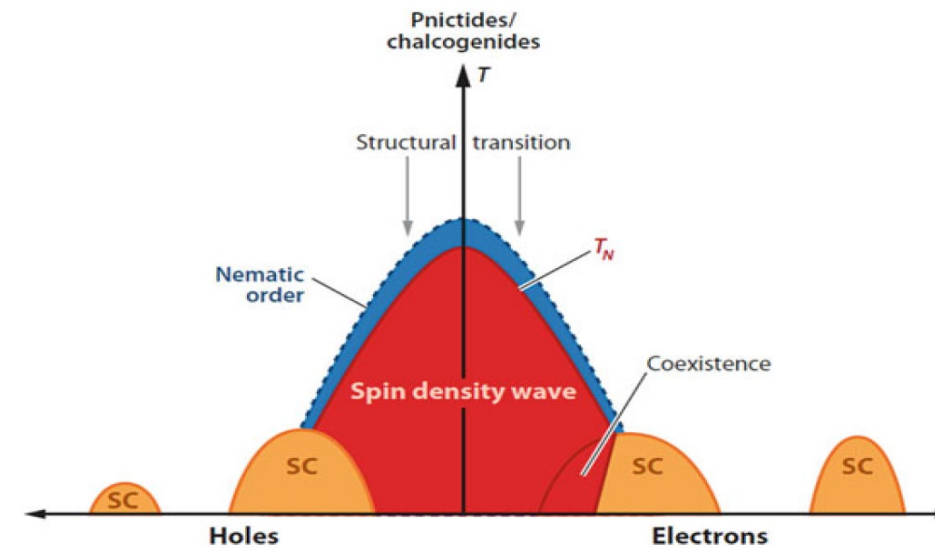
# Iron based high $T_c$ superconductors



❖ Various FBS Family

❖ Magnetic field response of FBS

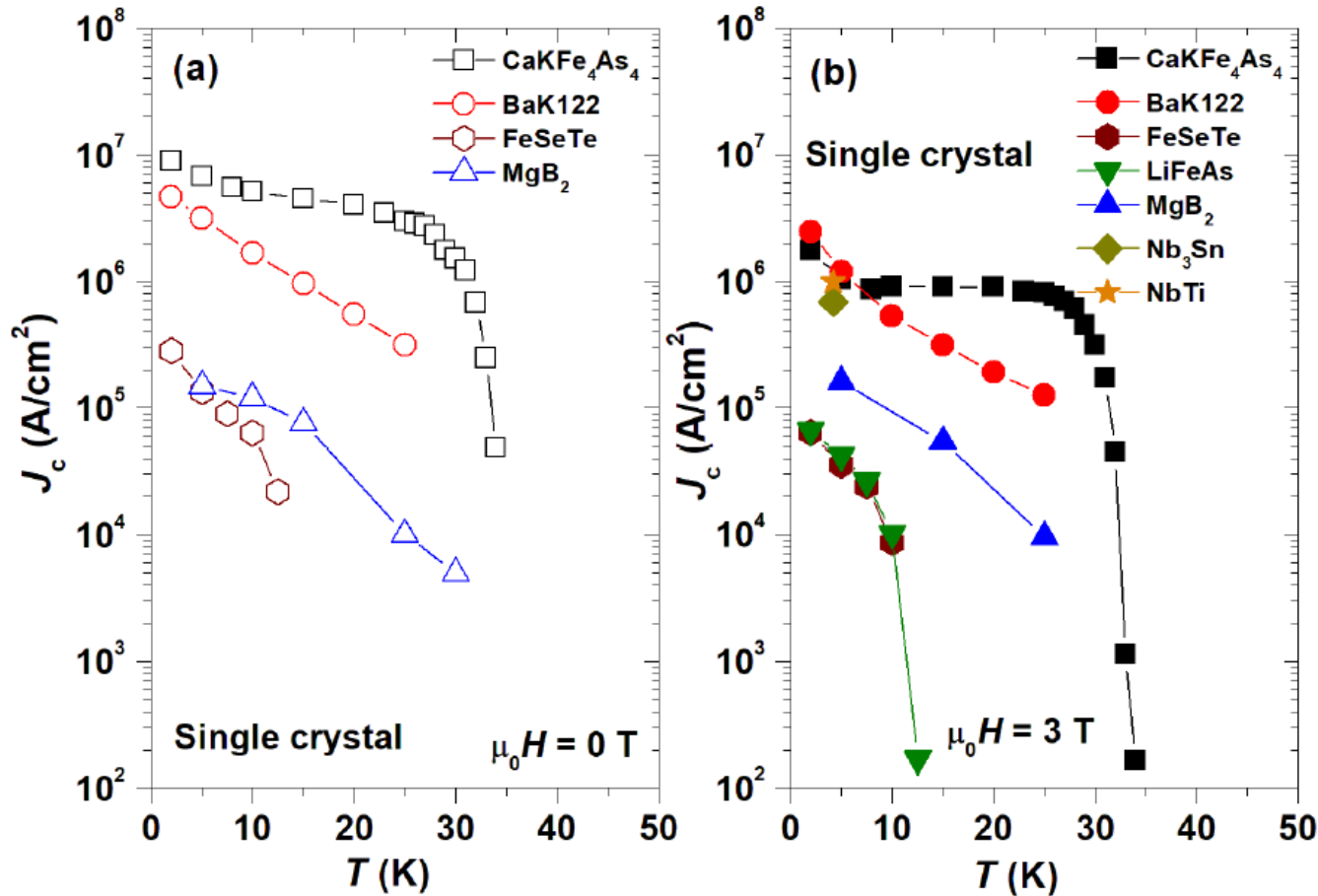
❖ Rich chemistry in FBS



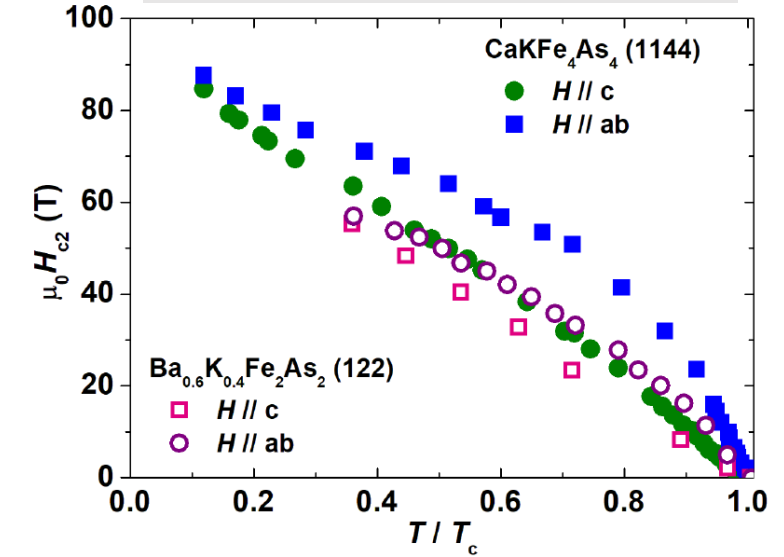
Shiv J. Singh et al. *Crystals* **12**, 20 (2022).  
S. J. Singh et al. *Phys. Rev. Mater.* **2**, 074802 (2018)

*Supercond. Sci. Tech.* **27**, 044002 (2014)  
*Supercond. Sci. Tech.* **25**, 113001 (2012)

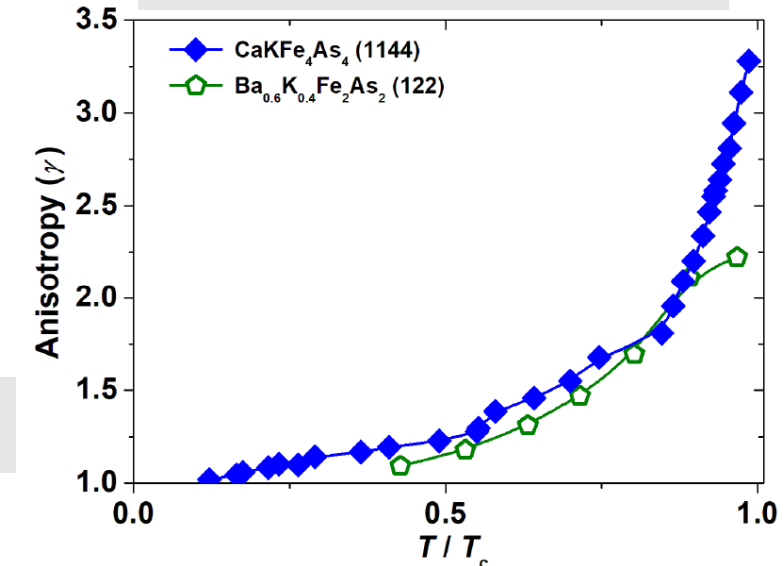
# Practical importance of iron-based high $T_c$ superconductors



## High upper critical field



## Low anisotropy of FBS



High critical current density of  $10^7$ - $10^8$  A/cm<sup>2</sup>

High upper field 100 T

Low anisotropy  $\sim$ 1-3

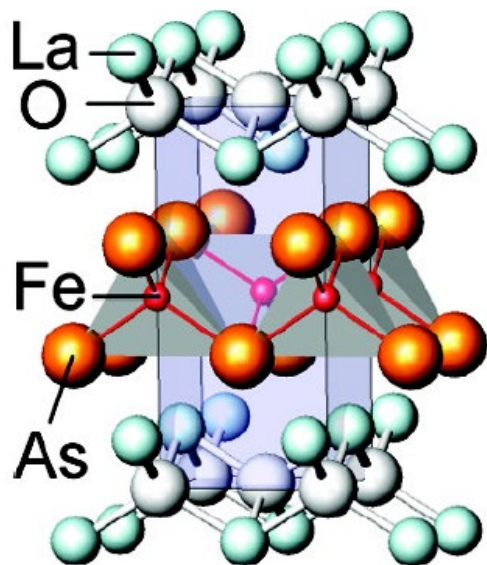
S. J. Singh et al., *Jenny Stanford Publishing*: New York, NY, USA, 2021; pp. 283–314.  
<https://doi.org/10.1201/9781003164685>

S. J. Singh et al. *Phys. Rev. Mater.* **2**, 074802 (2018).



# Two important families of iron based high $T_c$ superconductors

1111



- ❖ High transition temperature for FBS
- ❖ High critical current density for FBS
- ❖ High upper critical field

$REFeAsO$

$RE = La, Ce, Sm, Gd$

$T_c \sim 58 K$

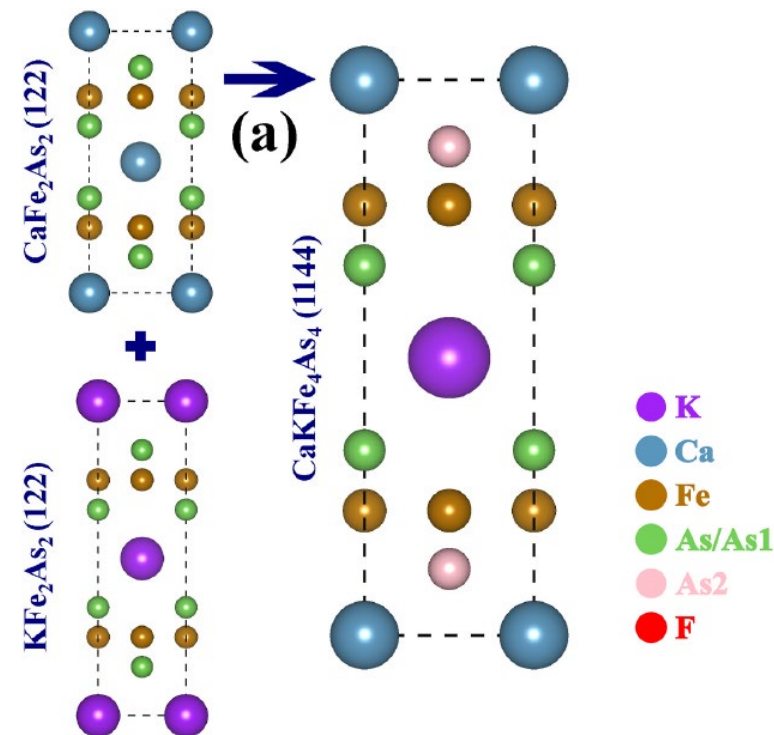
Doped superconductors

*J. Am. Chem. Soc.* **130**, 3296 (2008)

*J. Phys. Chem. Solids.* **160**, 110310 (2022)

High pressure growth technique is used to improve the sample quality and superconducting properties

1144



$AeAFe_4As_4$

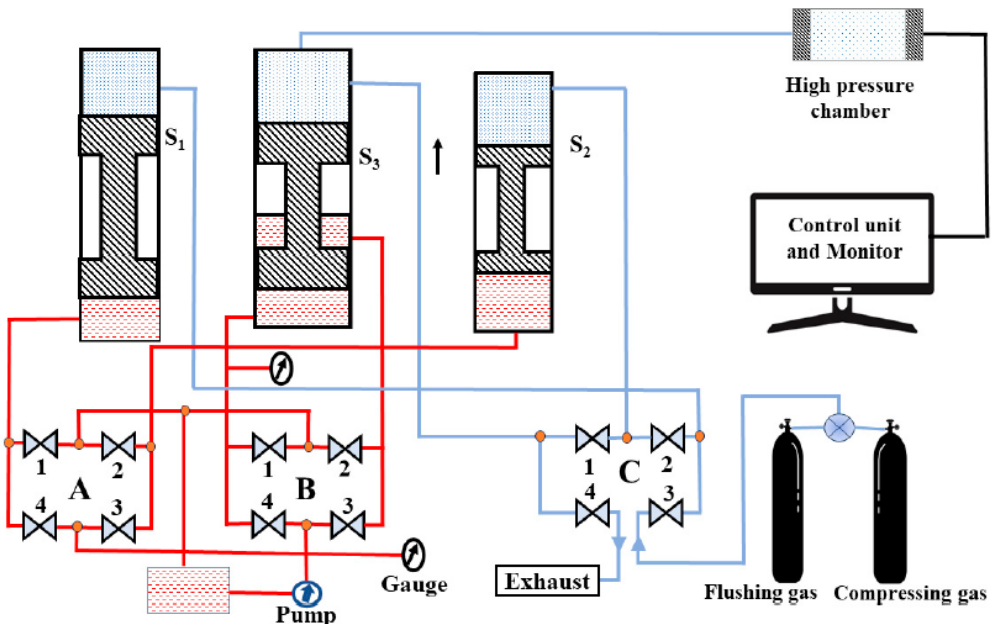
$Ae = Ca, Eu$  and  $A = K, Rb$

$T_c \sim 33-34 K$

Stoichiometric superconductors

- ❖ Comparative studies for doped and stoichiometric superconductors

## The block diagram



Sample holder



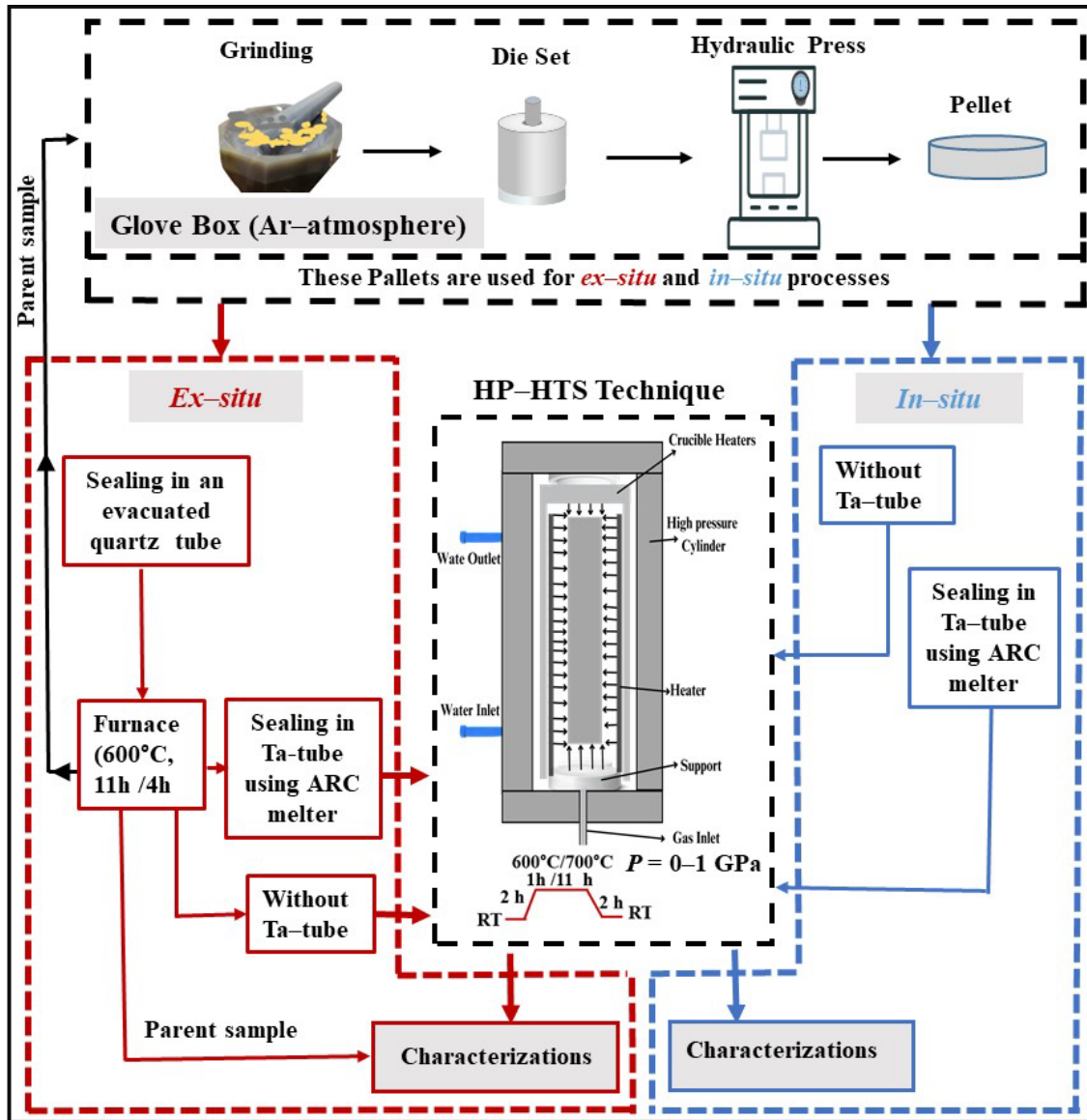
Compressor



Real pressure chamber

Azam et al. *Crystals* 13(10), 1525 (2023)

High gas pressure: up to 1.8 GPa and  
Heating temperature: up to 1700°C



❖ Need to optimize various parameters under high pressure growth:

- Growth pressure (0-1.8 GPa)
- Heating time
- In-situ process
- ex-situ process
- Sealed in Ta-tube
- Unsealed in Ta-tube
- Use of grinding and pelletized or powder

Azam et al. *Materials* **16**(15), 5358 (2023)

❖ To check reproducibility of each sample, at least two growth has been performed for each batch.



## ❖ High pressure growth of 1111

(1111:  $REFeAsO$ ,  $RE = La, Ce, Sm, Gd$ )

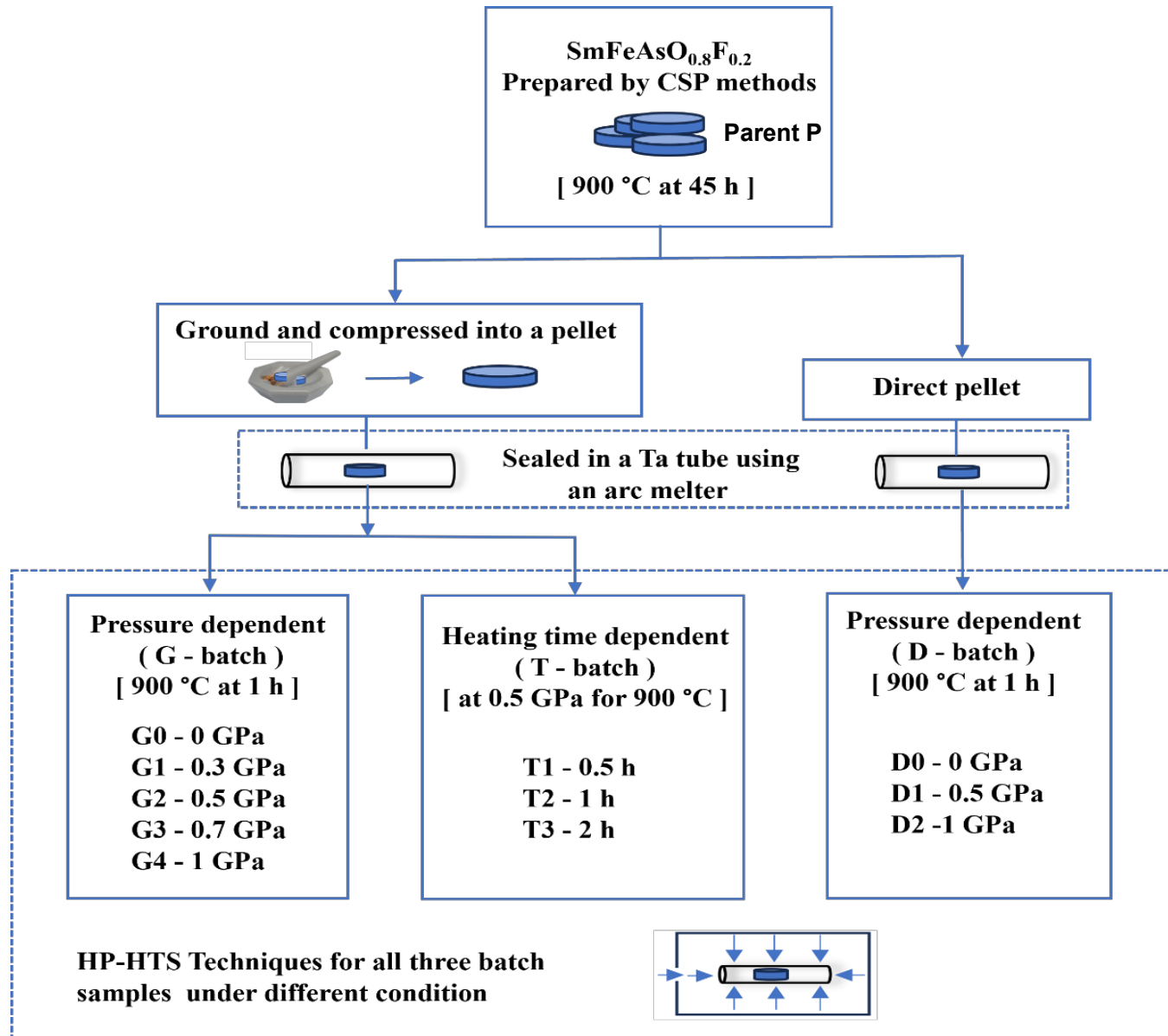
Azam et al. *et al.* Submitted to journal (under review ) (2024)

Azam et al. *et al.* *IEEE Trans. Appl. Supercond.* **34**, 7300205 (2024)

Azam et al. *et al.* *J. Am Ceram Soc.* 2024;1–15 (2024)



# High pressure growth of F doped SmFeAsO superconductor



- ❖ F doped Sm1111 (SmFeAsO<sub>0.8</sub>F<sub>0.2</sub>) prepared by Conventional Synthesis method at ambient pressure (CSP)  
(Sample P; Transition temperature  $T_c \sim 53$  K)

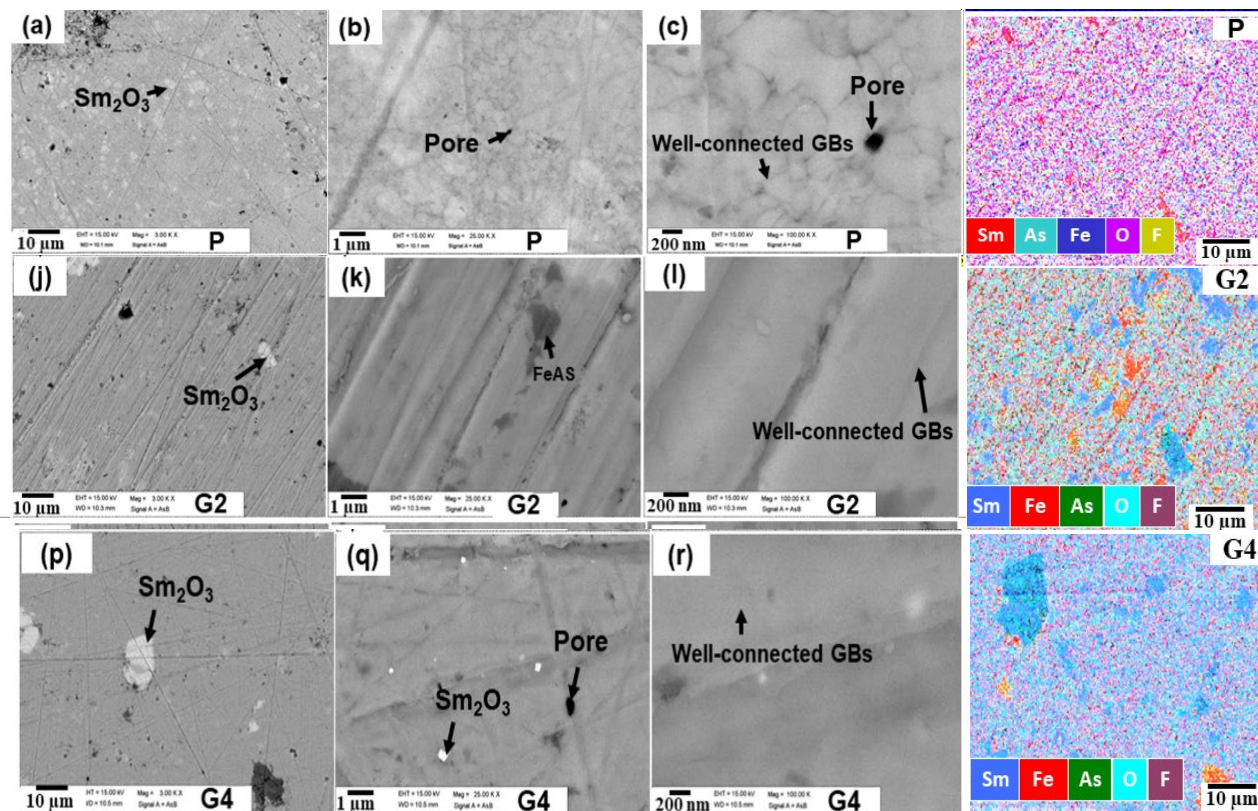
- ❖ Optimization of F doped Sm1111 by the high gas pressure growth of under various growth pressures (0–1.8 GPa).

- ❖ Grinded and pelletized condition  
Different pressure P: 0-1 GPa → **G-batch**  
Different heating time t : 0-2 hours → **T-batch**

and

- ❖ Direct pellet of the parent sample P  
Different pressure P: 0-1 GPa → **D-batch**

# High pressure growth of F doped SmFeAsO superconductor



**Parent**  
(P: 0 GPa)

❖ The impurity phase  $\text{Sm}_2\text{O}_3/\text{SmOF}$  are homogeneously distributed for the parent P by CSP. (Sample density ~ 50%)

**G-batch**  
G2: 0.5 GPa

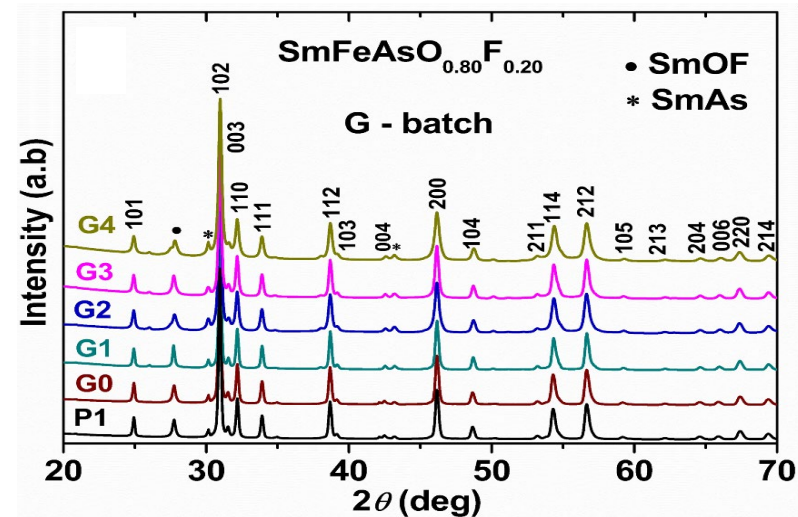
❖ The amount of this impurity phase is not changed with HP-HTS but accumulated many area. (Sample density ~ 59%)

**G-batch**  
G4: 1 GPa

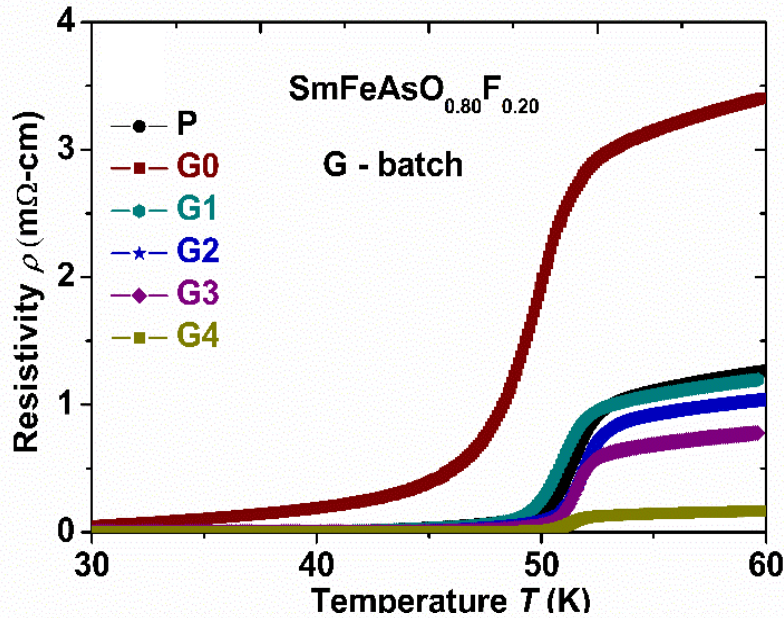
❖ This accumulation is more visible at higher pressure. (Sample density ~ 51%)

Azam et al. *et al.* Submitted to journal (under review ) (2024)

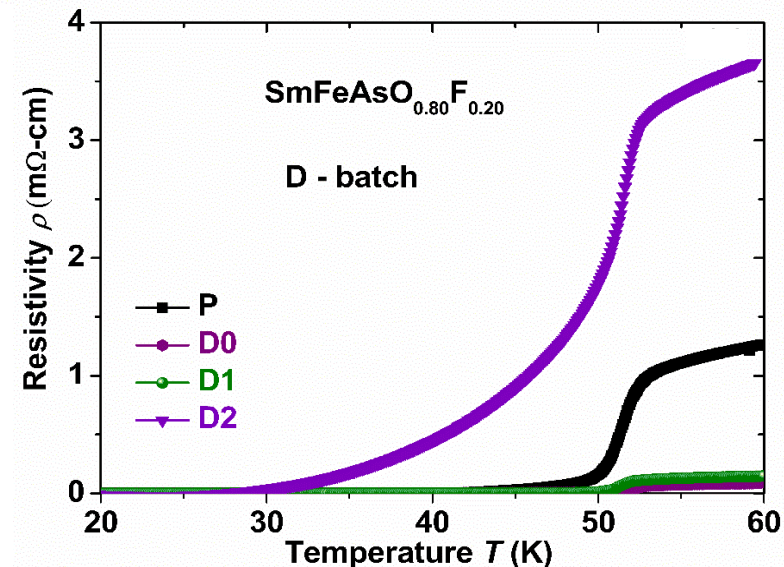
❖ The amount of the impurity phase is not changed with HP-HTS but accumulates in many areas.





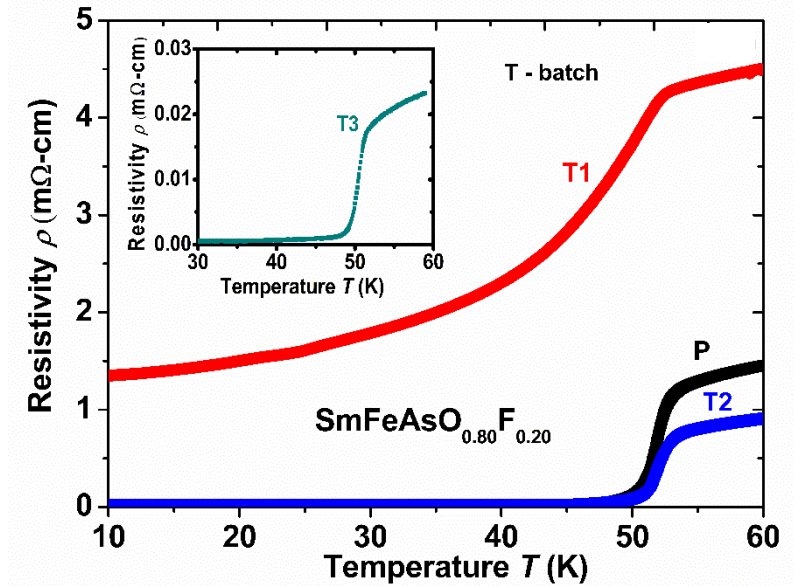


❖ For G-batch, the  $T_c^{onset}$  value is increased by  $\sim 1$  K for the growth pressure of 0.5 GPa.

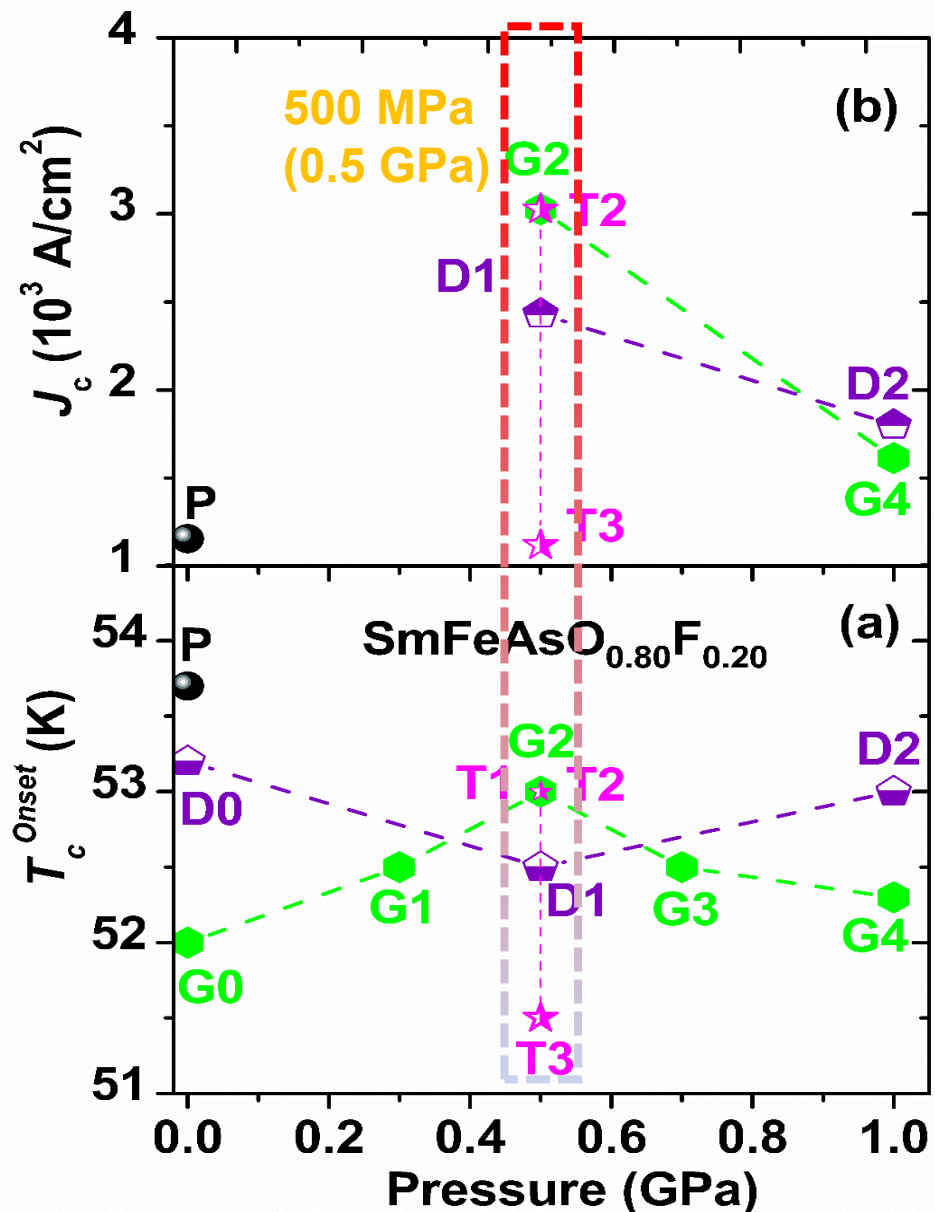


❖ For T-batch, the highest  $T_c^{onset}$  value is reached for heating time of 1 hour.

❖ For D-batch, a slight variation ( $\sim 0.5$  K) of  $T_c^{onset}$  value is observed for different growth pressures.



# High pressure growth of 1111 superconductor



- ❖ Highest  $T_c^{onset}$  value for the sample G2 (grinded and pelletized) i.e. the growth pressure of 0.5 GPa
- ❖ Slightly lower  $T_c^{onset}$  for the D1 (direct pellet) prepared at 0.5 GPa
- ❖ Long heated sample T3 (Long heating time: 2 h), Lower  $T_c^{onset} \sim 51 \text{ K}$
- ❖ The samples prepared at 0.5 GPa has shown the high  $J_c$  value than the parent P and other samples

Azam et al. *et al.* Submitted to journal (under review ) (2024)

- ❖ **The optimal growth pressure: 0.5 GPa, 900°C, 1 h**  
Grinded and pelletized parent P

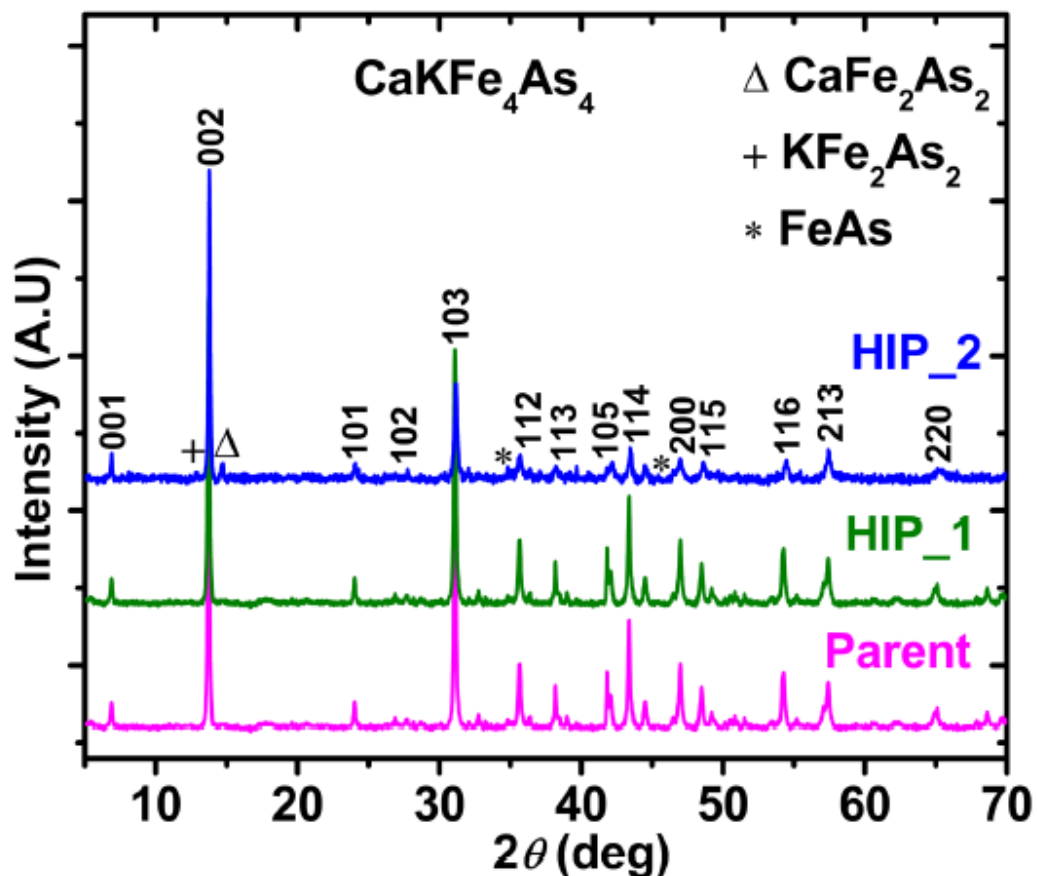


## ❖ High pressure growth of 1144: $\text{CaKFe}_4\text{As}_4$

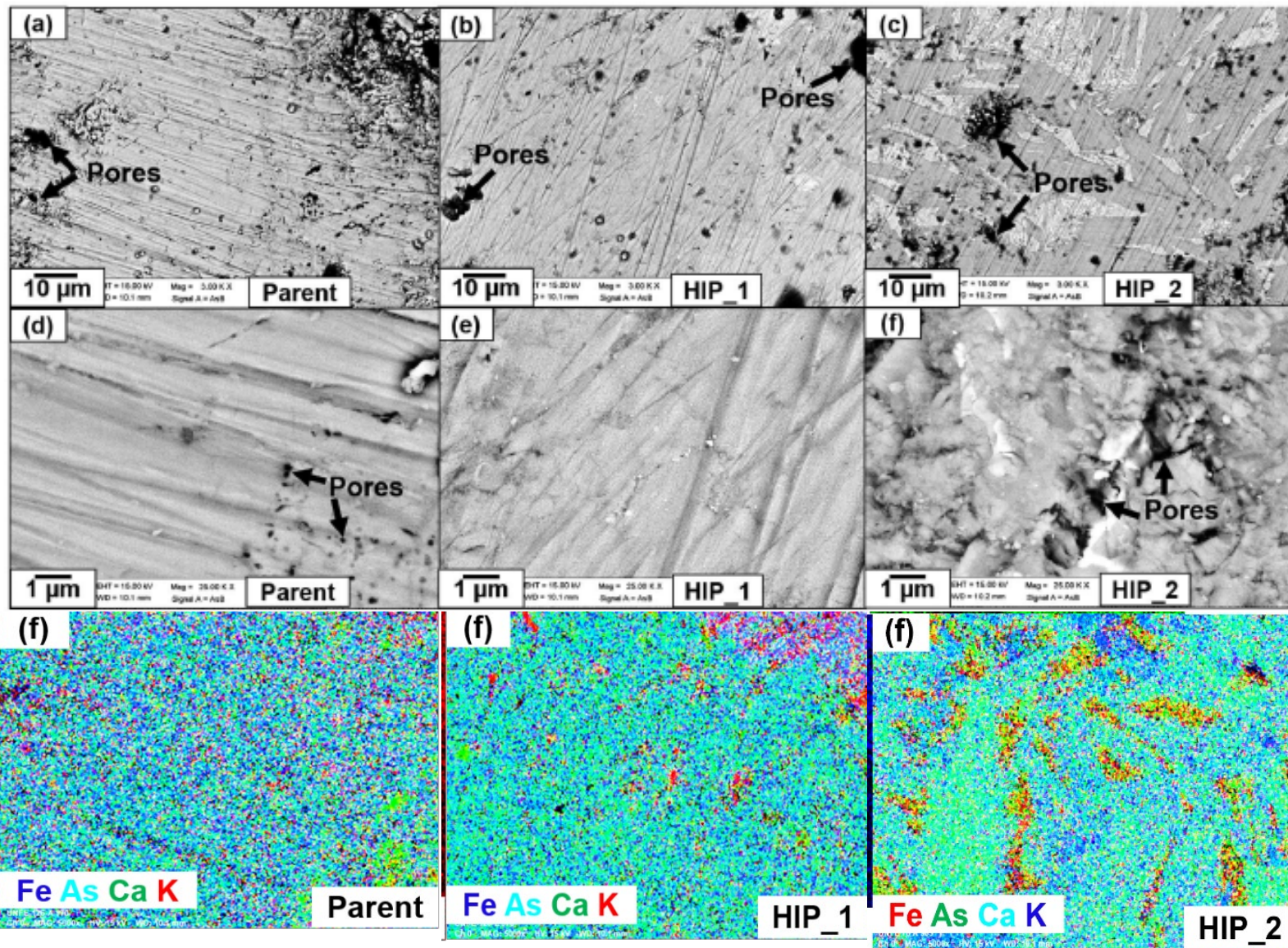
Manasa et al. *IEEE Trans. Appl. Supercond.* **34**, 7300605 (2024)

Manasa et al. *Ceramics International* **50**, 714-72 (2024)

Manasa et al. *J. Phys. Chem. Solids.* **190**, 111996 (2024)



- ❖ **Parent: 0 GPa**  
**HIP\_1: 500 MPa** (open in Ta-tube)  
**HIP\_2: 500 MPa, 1 h** (sealed in Ta-tube)
- ❖ XRD analysis confirms the tetragonal phase with space group *I4/mmm* (ThCr<sub>2</sub>Si<sub>2</sub>-type structure)
- ❖ **Parent and HIP\_1 have a clean 1144 phase** and no impurity phase was observed.
- ❖ A small amount of CaFe<sub>2</sub>As<sub>2</sub> is detected together with a tiny amount of FeAs for HIP\_2.



- ❖ The parent and HIP\_1 have almost homogeneous microstructures.
- ❖ It seems that HIP\_1 has many well-connected grain boundaries (GBs) and is more compact compared to the parent compound.
- ❖ However, many pores do exist in the parent compared to HIP\_1.

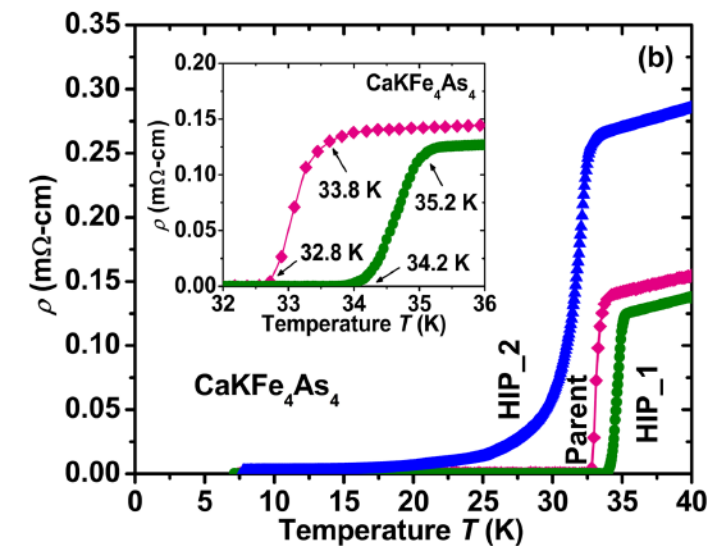
Manasa et al. *J. Phys. Chem. Solids.* **190**, 111996 (2024)

- ❖ In the case of HIP\_2, it appears that grain connections are reduced rapidly and pore sizes are increased

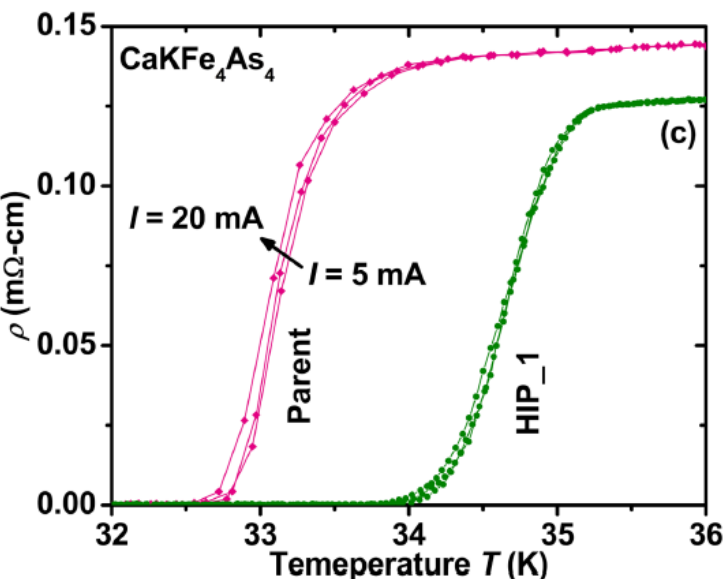
Manasa et al. *IEEE Trans. Appl. Supercond.* **34**, 7300605 (2024)



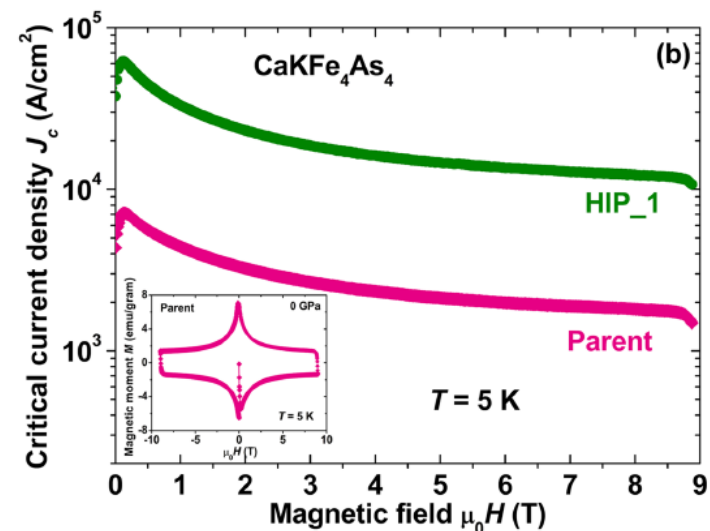
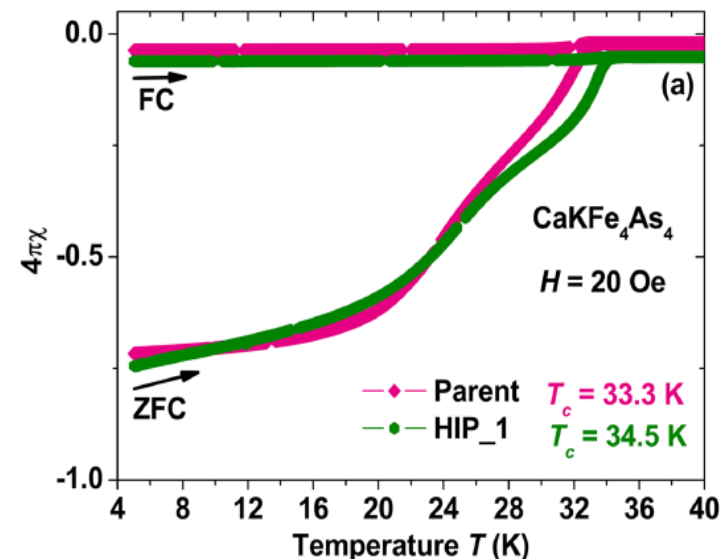
# High pressure growth of stoichiometric 1144 superconductor



- ❖ The parent compound:  $T_c^{onset} = 33.8$  K with  $\Delta T \sim 1$  K
- ❖ HIP\_1 sample:  $T_c^{onset} = 35.2$  K with  $\Delta T \sim 1$  K comparable to that of 1144 single crystal.

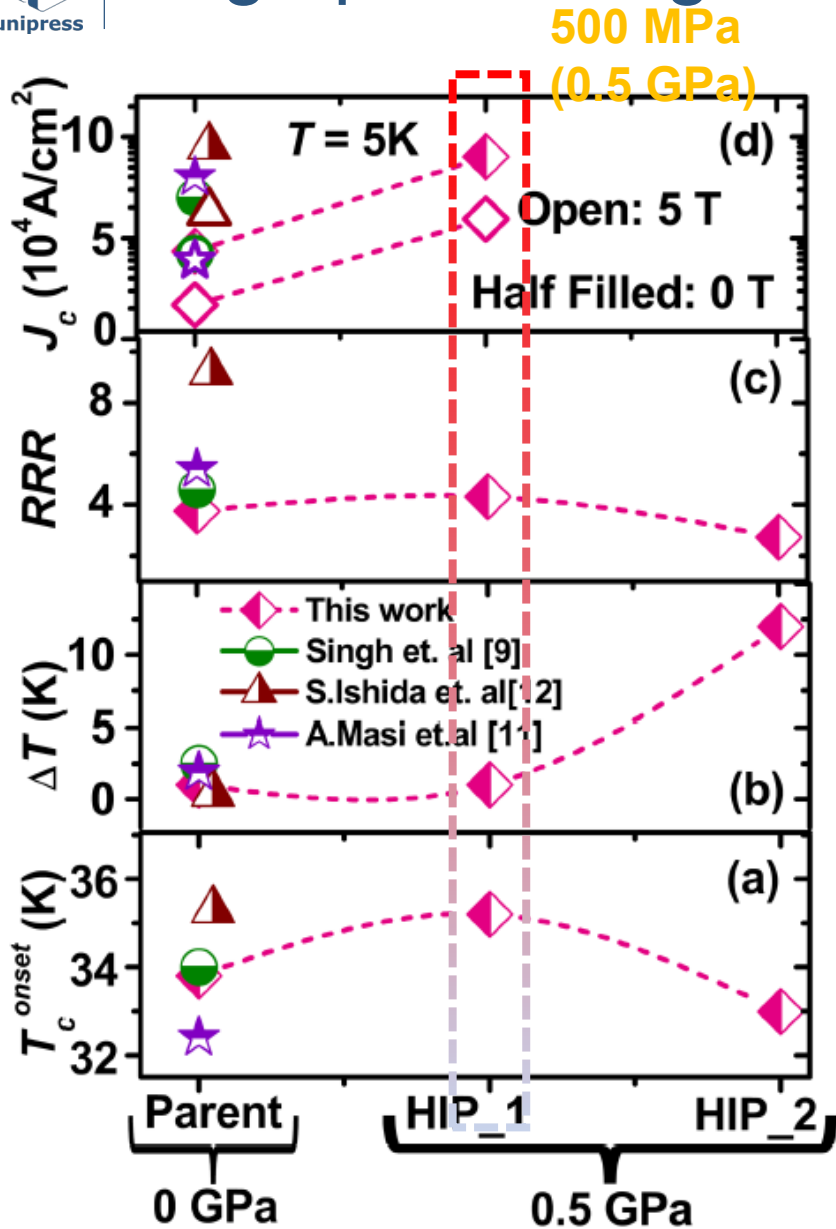


- ❖ The sharper transition suggest better grain connections.
- ❖ By the high-pressure synthesis method, the  $J_c$  value is enhanced by one order of magnitude compared to the parent sample.





# High pressure growth of stoichiometric 1144 superconductor



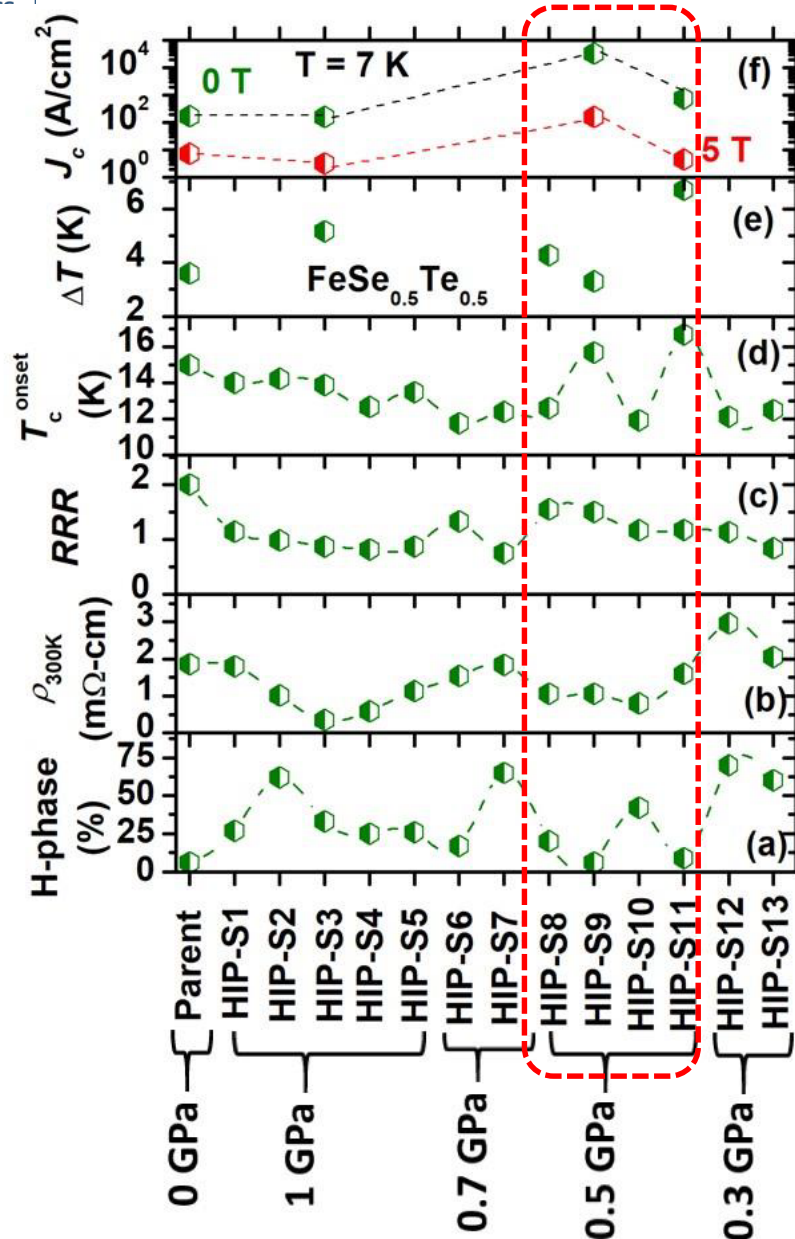
- ❖ HIP\_1 has a slightly improved  $RRR$  value (4.3) than that (3.7) of the parent sample, suggesting a homogeneous and good-quality of HIP\_1 sample compared to our other samples.
  - ❖ Interestingly, HIP\_1 has enhanced the  $J_c$  value in the whole magnetic field up to 9 T compared to the parent samples.
- Manasa et al. *J. Phys. Chem. Solids.* **190**, 111996 (2024)
- ❖ This value is almost the same as a value reported for 1144 prepared by CSP [9] [11] at ambient pressure and SPS [12].
  - ❖ **CaKFe<sub>4</sub>As<sub>4</sub> prepared at 0.5 GPa by HP-HTS into an open Ta-tube exhibits high superconducting properties with the improved sample quality.**
  - ❖ **Our study confirm that high-pressure synthesis has worked well for the 1144 family.**

## ❖ High pressure growth of Fe(Se,Te) (11) family

Manasa *et al.* *Ceramics International* **50**, 714-72 (2024)

Azam *et al.* *Materials* **16**(15), 5358 (2023)

# High pressure growth of $\text{FeSe}_{0.5}\text{Te}_{0.5}$ by HP-HTS



- ❖ Hexagonal phase reached its lowest level for the samples prepared at 500 MPa for 1 h with sealing into a Ta-tube.
- ❖  **$\text{FeSe}_{0.5}\text{Te}_{0.5}$  sample sealed into a Ta-tube** is more effective for the enhancement of sample density and the improvement in grain connectivity.
- ❖ Although the existence of a hexagonal phase depending on the pressure synthesis conditions reduces the superconducting grain connections.

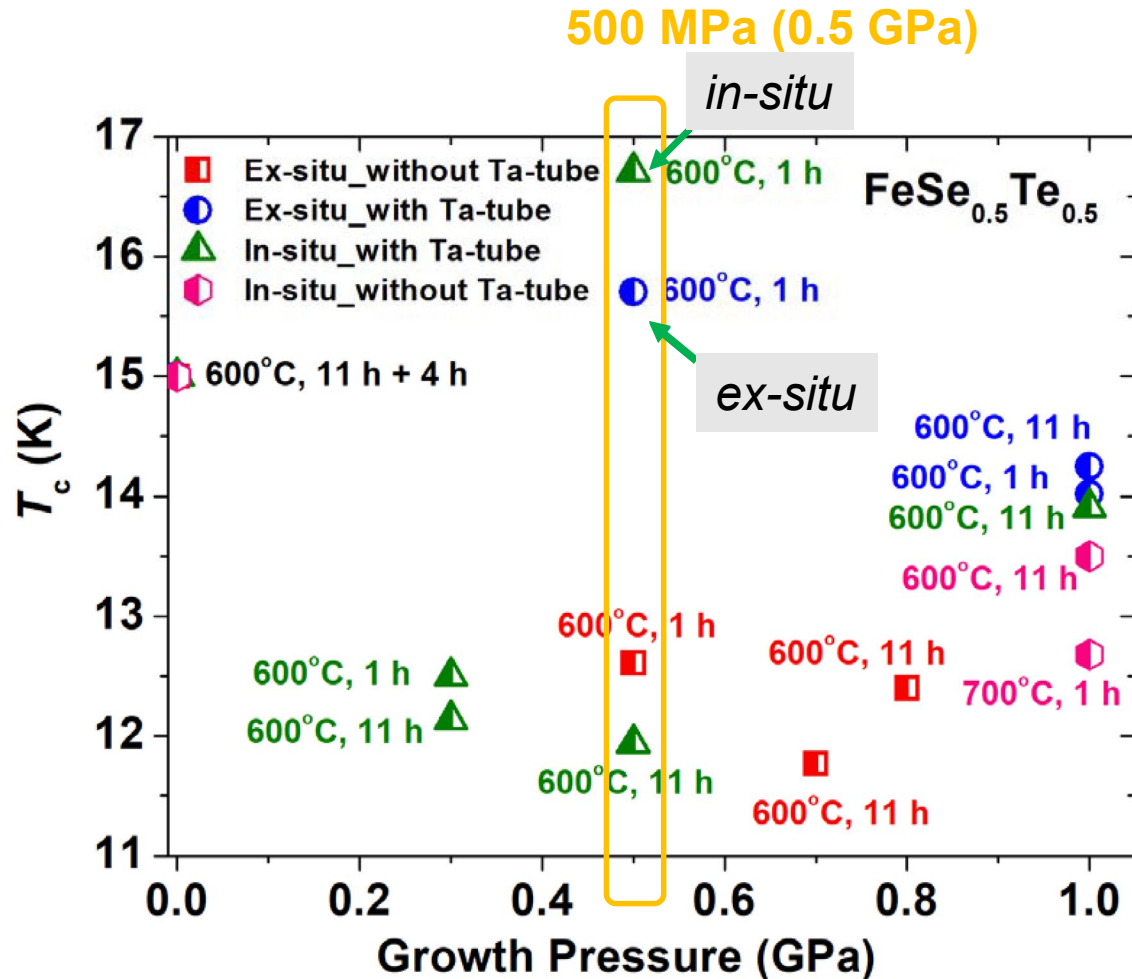
Manasa et al. *Ceramics International* **50**, 714-72 (2024)

### Editor's Choice

M. Azam, M. Manasa, T. Zajarniuk, R. Diduszko, T. Cetner, A. Morawski, A. Wiśniewski, S. J. Singh, *Materials* **16**(15), 5358 (2023)

S. J. Singh et al.. *Appl. Phys. A* **128**, 476 (2022)

# 11 family: $\text{FeSe}_{0.5}\text{Te}_{0.5}$ by HP-HTS



- ❖ The enhancement of the transition temperature by 2 K for  $\text{FeSe}_{0.5}\text{Te}_{0.5}$  prepared at 500 MPa.
- ❖ **Optimum high-pressure growth conditions are 500 MPa, 600°C, a heating time of 1 h, and the sample sealed in a Ta-tube,**
- ❖ ***In-situ* process: sufficient for the development of the tetragonal phase formation, and**
- ❖ ***Ex-situ* process: contributes to the improvement in the intergrain connections and also promotes the formation of the superconducting phase.**

Manasa et al. *Ceramics International* **50**, 714-72 (2024)

Editor's Choice

M. Azam, M. Manasa, T. Zajarniuk, R. Diduszko, T. Cetner, A. Morawski, A. Wiśniewski, S. J. Singh  
*Materials* **16**(15), 5358 (2023)



- ❖ High pressure synthesis is an effective way to enhance the sample quality and superconducting properties of high  $T_c$  iron based superconductors.
- ❖ **The high-pressure synthesis of these samples has enhanced the  $T_c$  by 2-3 K for  $\text{CaKFe}_4\text{As}_4$  and  $\text{Fe}(\text{Se},\text{Te})$  bulks, whereas it is almost constant for the 1111 family.**
- ❖ The sample quality, sample density, and grain connections of all these FBS families have improved, and their  $J_c$  value has increased by one order of magnitude ( $10^4$ - $10^5$  A/cm<sup>2</sup>, 5 K, 0 T) compared to that of CSP ( $10^2$ - $10^3$  A/cm<sup>2</sup>, 5 K, 0 T).
- ❖ A growth pressure of 0.5 GPa and a short heating time (~1 hour) are sufficient and work well as optimal conditions for various families of FBS.
- ❖ **High-pressure growth works well for various FBS, and more research is demanded in this direction.**

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Faculty of Physics, Warsaw University of Technology, Warsaw, Poland

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**Thank you very much for your attention**