



Italian National Agency for New Technologies,
Energy and Sustainable Economic Development



Recent activities on REBCO and IBS materials at ENEA

Andrea Augieri
(on behalf of the ENEA HTS group)

HFM annual meeting 2023 – October 31, 2023



Outline

Brief introduction on the ENEA Superconductivity Laboratory

Activities on REBCO

- Film nano-engineering (APC)
- Irradiation tests on REBCO
- HTS Cables

IBS Materials

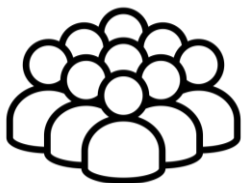
- 11-coated conductors
- PIT wires

Conclusions and perspectives

ENEA Superconductivity Laboratory

The Superconductivity group

28 people



23 Researchers



4 Technicians



1 Administrative

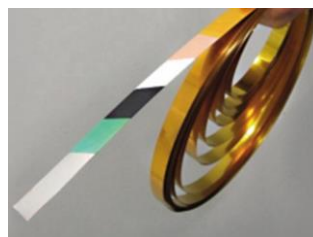


LTS group: 5 Engineers + 6 Physicists

Nb-alloys R&D;
LTS Cable design and manufacturing;
High field magnets design



Close collaboration on
HTS cable activities

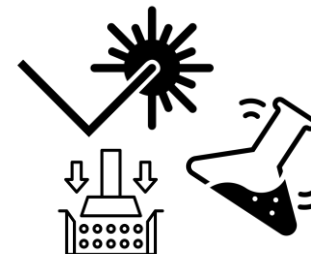


HTS group: 9 Physicists + 2 Chemists + 1 Engineer

Coated-Conductor R&D;
REBCO deposition and optimization;
HTS Cable design and manufacturing;
IBS materials R&D

ENEA Superconductivity Laboratory

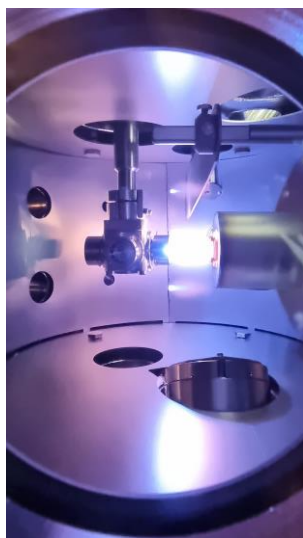
The Superconductivity laboratory equipment: material synthesis



PVD systems

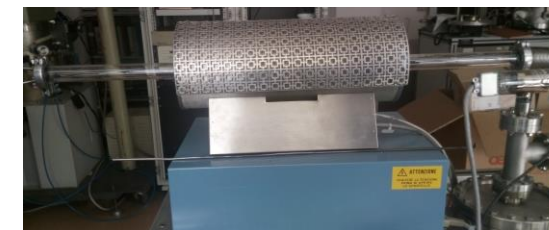
3 PLD systems
operating with 2 Lasers
(KrF and Nd-YAG)

2 e-beam systems



CSD systems

Chemical lab for MOD
(furnaces, evaporator, spinner, ...)



Material sintering systems

(Grinding, milling, glow boxes,
controlled ovens, ...)

ENEA Superconductivity Laboratory

The Superconductivity laboratory equipment: characterizations



Structural-Morphological characterizations

Two XRD
SEM with EBSD and EDX
AFM

Electro-magnetic characterizations

VSM system (12 T)

3 A d.c. current system, (12 T)

18 T cryo-free system (VSM, d.c. current 3 A, χ_{ac})

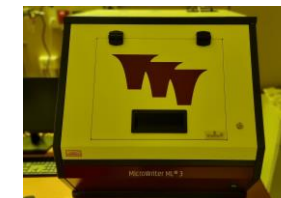
14 T cryostat with 2 d.c. current probes

“walter spring” for wires (1000 A)
d.c. current for tapes up to 1500 A



Laser writer

For sample
patterning



High-current station for HTS
cable characterization at LN2

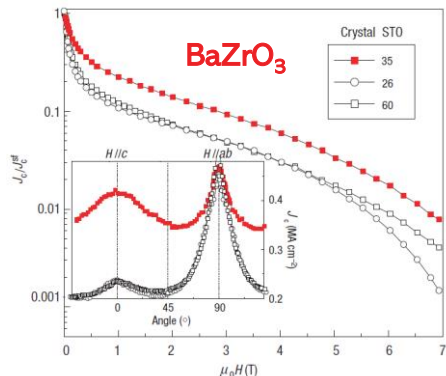
Self-Field I - V up to 20 kA

Activities on REBCO

- Film nano-engineering (APC)
- Irradiation tests on REBCO
- HTS Cables

Film nano-engineering (APC)

Controlled introduction of nano-metric Artificial Pinning Sites (APC)

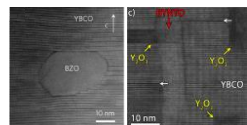


J. L. Macmanus-Driscoll *et al.*,
Nature Materials **3** (2004)

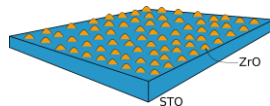


Different Methods

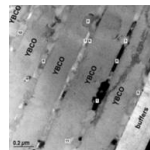
Second phases
(Y₂O₃, BaMO₃, ...)



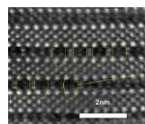
Surface decoration



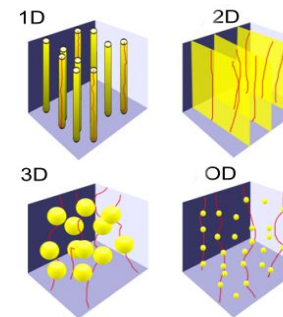
(quasi) Multi-layers



Crystalline defects



Different shapes and densities



Made possible
the use of CCs
in High Field
Magnets

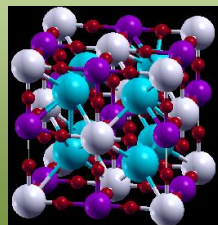


Is active on the APC topic since the very beginning, using different methods and materials

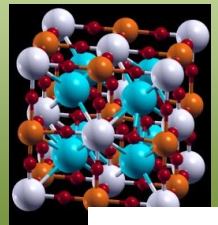
Main activity:

PLD REBCO films
with
Double perovskite
cubic - Fm3m

Ba₂YNbO₆



Ba₂YTaO₆



Task n.: AWP15-ENR-01-ENEA 08

Task n.: AWP19-ENR-01-ENEA 04

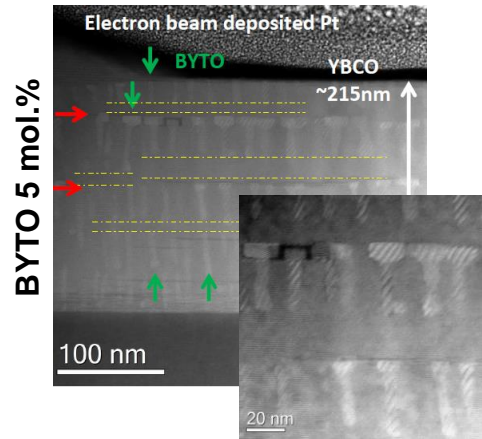
Enabling Research Work Programme
2015-2017 and 2019-2020



Film nano-engineering (BYNTO)

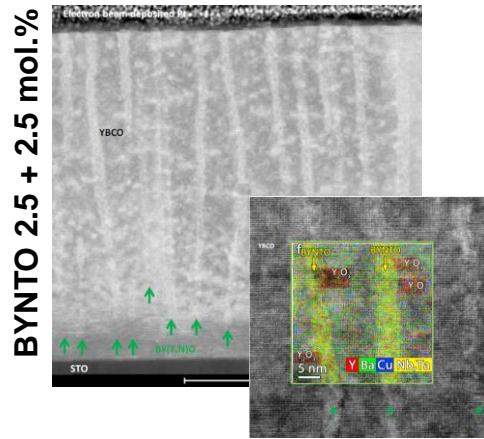
Composition

Ba_2YNbO_6 or Ba_2YTaO_6



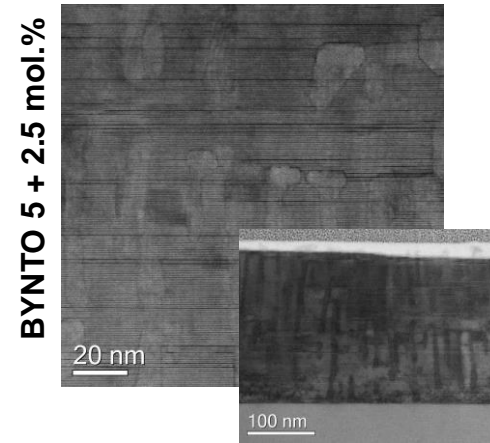
$\varnothing = 5 \text{ nm } B_\phi = 5.2 \text{ T}$

$Ba_2YNbO_6 + Ba_2YTaO_6$



$\varnothing = 5 \text{ nm } B_\phi = 5.2 \text{ T}$

$Ba_2YNbO_6 + Ba_2YTaO_6$ unbalanced



$\varnothing = 10 \text{ nm } B_\phi = 7.1 \text{ T}$

And others

- BYNTO+ Y_2O_3
- total doping up to 15 mol.%
- different unbalance degree
- ...

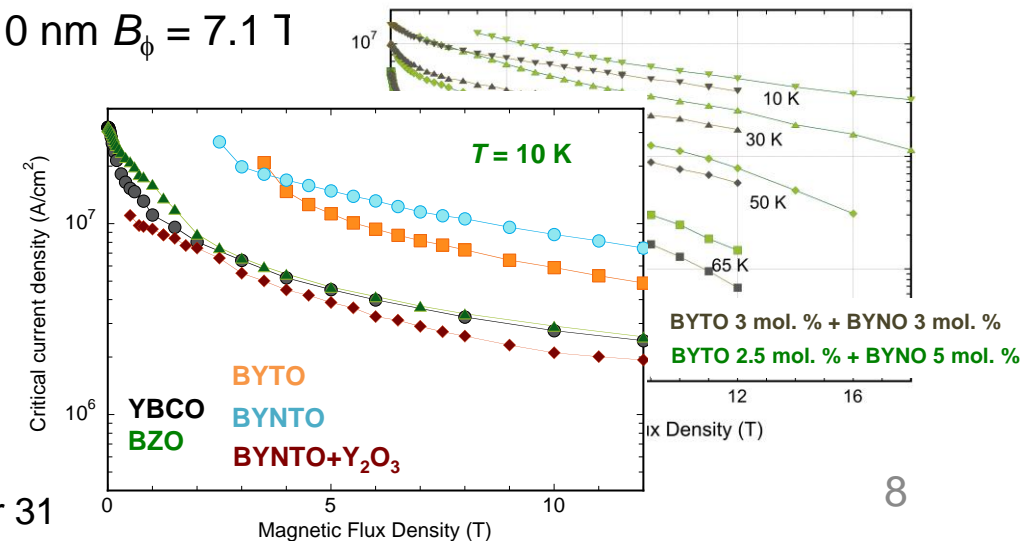
Playing with the second phase composition



Tuning of the film micro-structure



Change in the film performances



Film nano-engineering (APC)

Deposition parameters

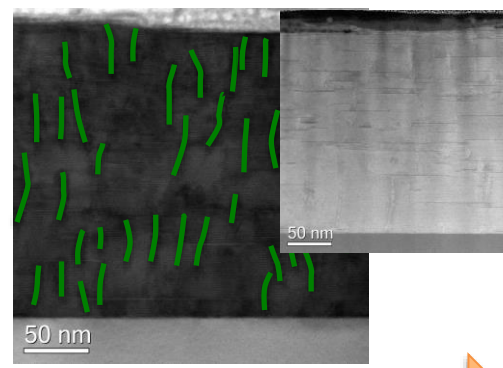
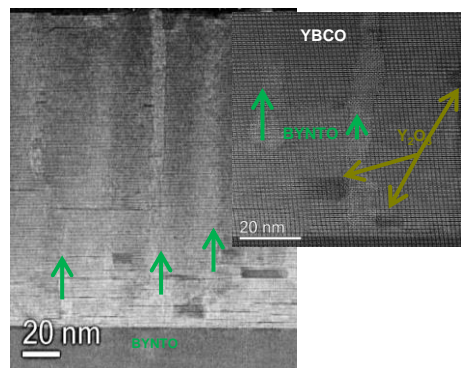
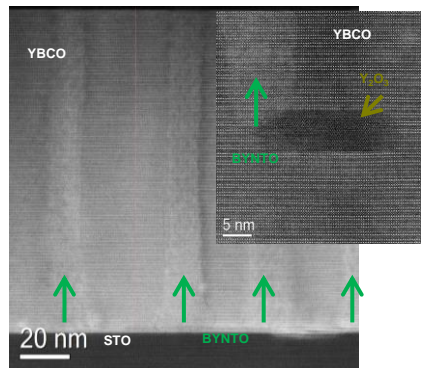
2.5 mol.% Ba₂YNbO₆ + 2.5 mol.% Ba₂YTaO₆

Laser wavelength (308 nm, 248 nm)

Laser rep. rate (1 Hz – 15 Hz)



Growth rate $\rho \approx 0.02 \div 1.8 \text{ nm s}^{-1}$



Increasing the growth rate

Reduced column

- diameter
- continuity
- straightness

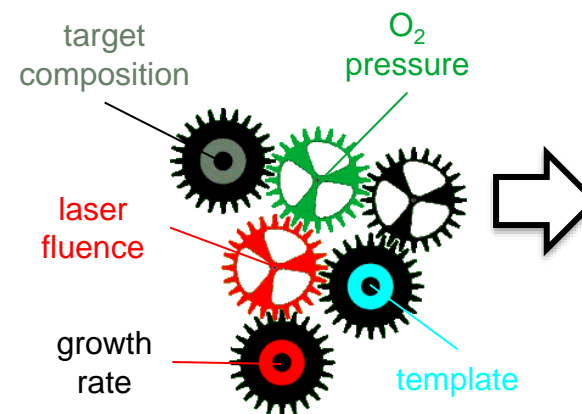
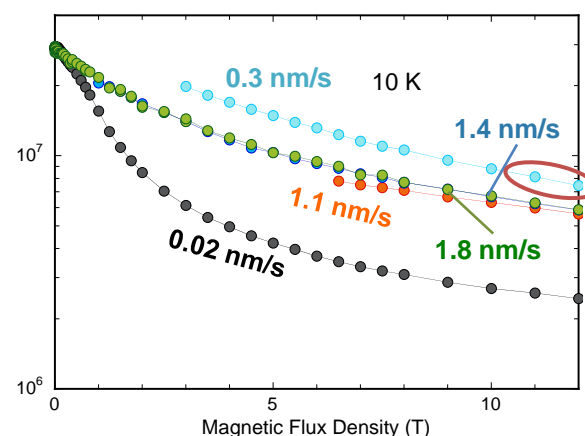
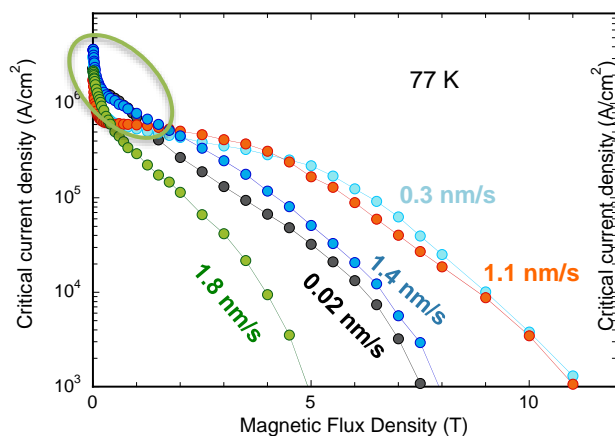
Increase density of Stacking faults

F. Rizzo et al., Nanoscale 10, (2018)

$\rho = 0.02 \text{ nm/s}$

$\rho = 0.1 \text{ nm/s}$

$\rho = 1.8 \text{ nm/s}$



Optimization for different applications

Activities on REBCO

- Film nano-engineering (APC)
- Irradiation tests on REBCO
- HTS Cables

14 MeV neutron irradiation test

ENEA-Frascati Neutron Generator



Irradiation of REBCO films with 14 MeV Neutrons

PLD YBCO films

MOD YBCO films
(on STO and LAO)

Commercial CCs
(SST and SO)

1 dose:
 $0.4 \cdot 10^{14}$
neutrons·cm⁻²

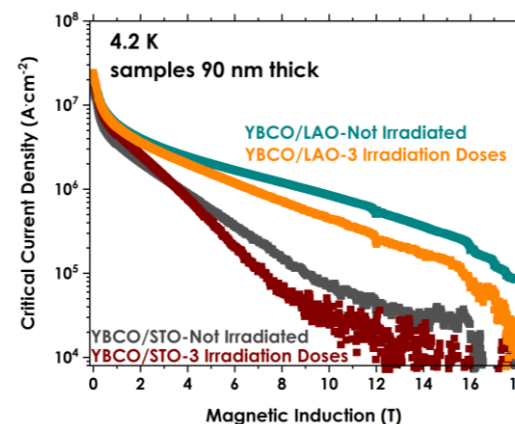
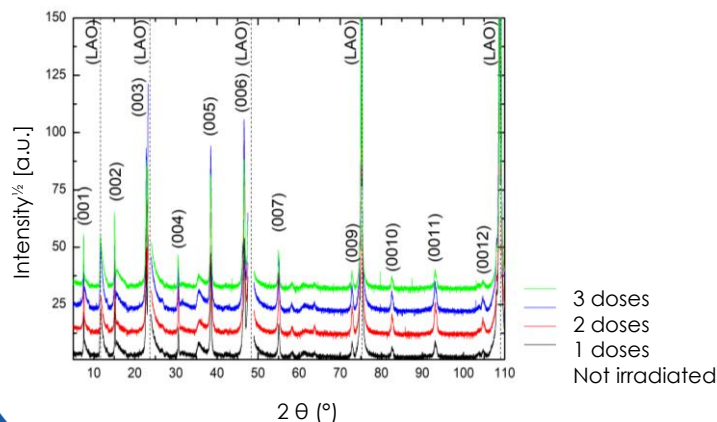
2 doses:
 $0.8 \cdot 10^{14}$
neutrons·cm⁻²

3 doses:
 $1.2 \cdot 10^{14}$
neutrons·cm⁻²

72h of ITER
plasma on TF

Preliminary results

No detectable
difference on
structural
properties

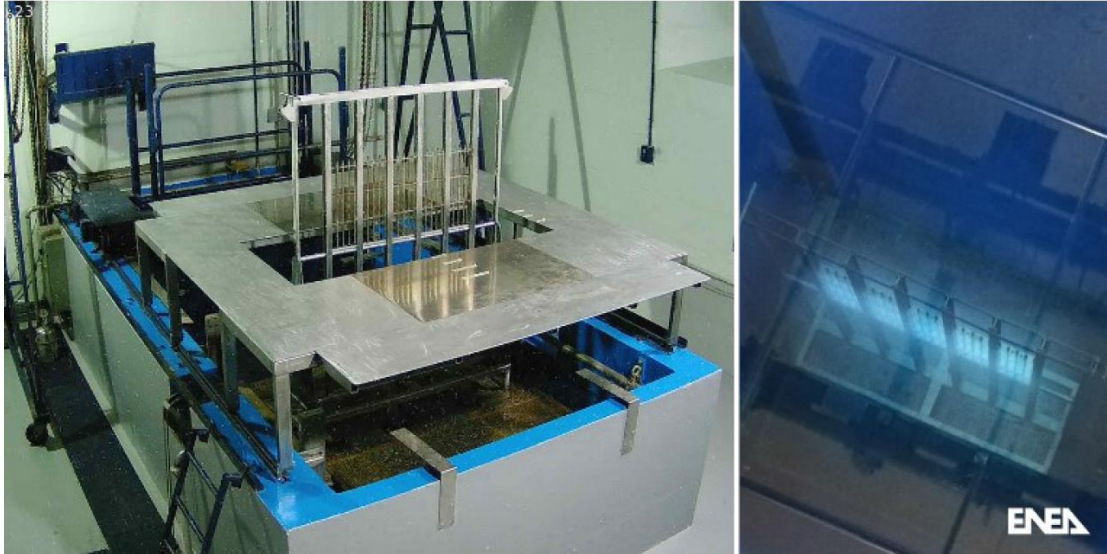


Slight decrease
of the in-field
properties

To do list

- ✓ Increase the neutrons dose
- ✓ Superconducting properties test during irradiation

γ -Irradiation test



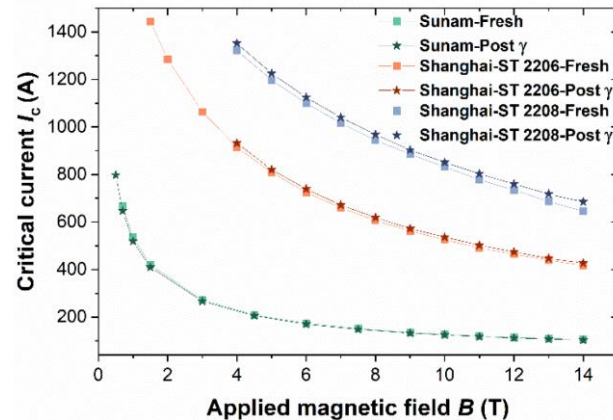
Calliope test facility at ENEA

Features	
Source	^{60}Co , stainless steel double encapsulated rod
Geometry	Plane rack
Emitted radiation	2 photons emitted in coincidence
Mean photon energy	1.25 MeV
Max licensed activity	$3.70 \cdot 10^{15}$ Bq (100 kCi)
Max dose rate (June 2023)	6.5 kGy/h

**Commercial CCs
4 mm wide
with Ag and Cu layers**

- Sunam
- SST
- SuperOx

**Preliminary results
on 1.016 kGy
adsorbed dose
(relevant for space
applications)**



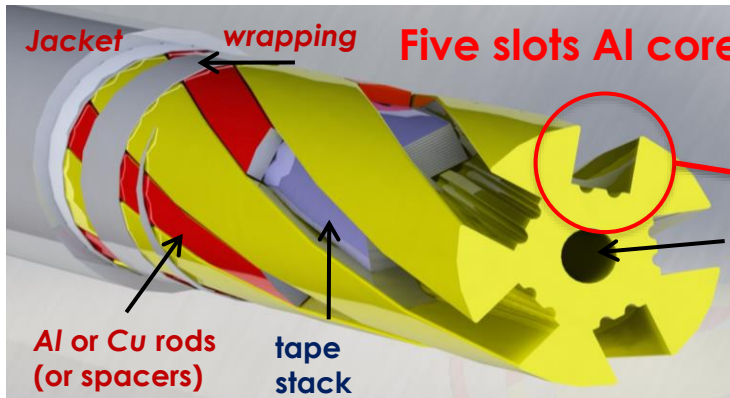
**No evident effect
on the tapes in-
field properties**



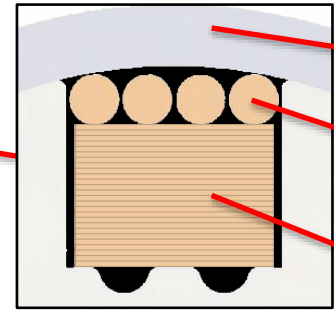
Activities on REBCO

- Film nano-engineering (APC)
- Irradiation tests on REBCO
- HTS Cables

ENEA HTS Cable – historical overview



5 slots $4.3 \times 4.3 \text{ mm}^2$



Jacket
Filler
Tapes stack (20 or 30)

20 kA – class cable for Fusion applications (4.2 K - 12 T)

360 mm² cross section

Al core: $\varnothing = 19 \text{ mm}$
Al or SS jacket: $t = 1.2 \text{ mm}$

$J_e \approx 60 \text{ A/mm}^2$

G. Celentano et al., *IEEE Trans. Appl. Supercond.* 24 (2014)

Cable design driven by industrial scalability

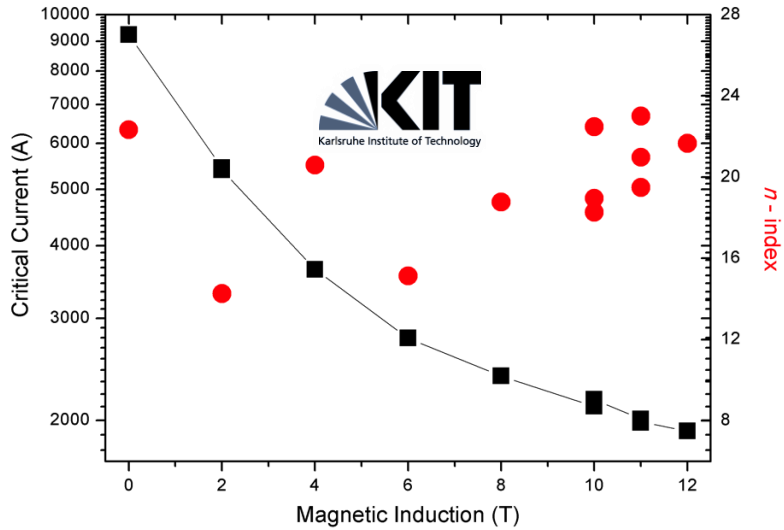


Operation ready cable



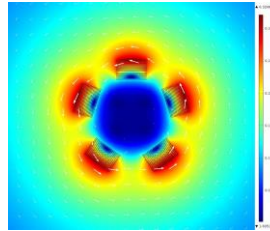
ENEA HTS Cable – historical overview

Test at LHe $B \parallel c$ -axis

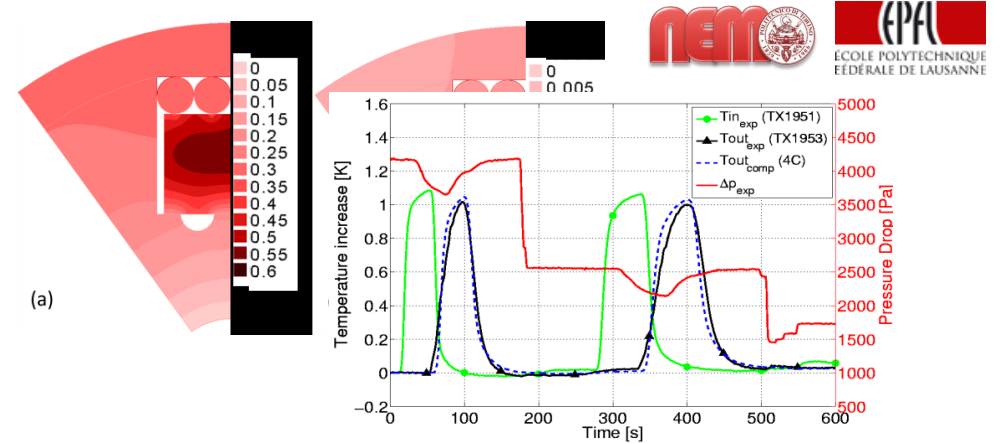


Stack $I_c = 1952$ A 12 T
(using Sunam Tapes)

Predicted Cable I_c at
12 T **8970 A**
(20 kA using SPI)

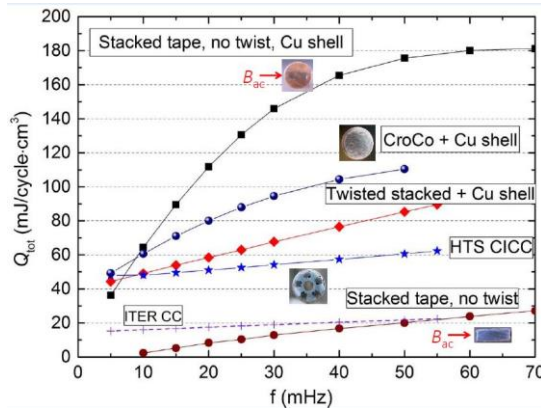


Thermal-hydraulic test

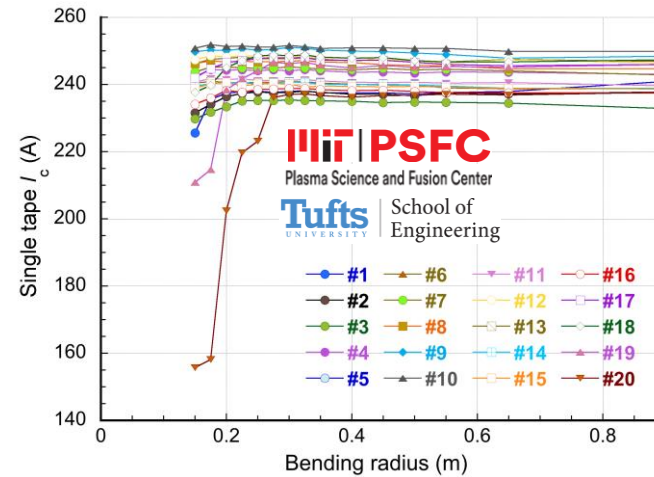
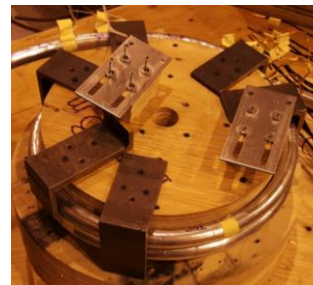


A. Augieri et al., *IEEE Trans. Appl. Supercond.* **25** (2015)

a.c. losses



Bending test



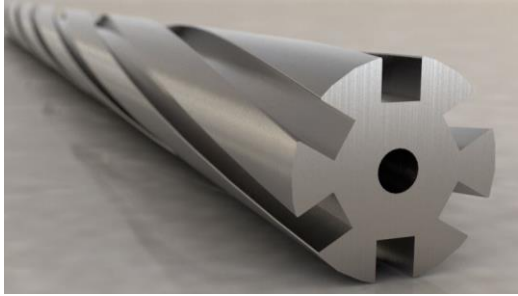
Cable properties fully assessed



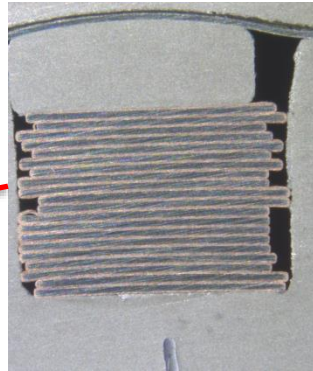
G. De Marzi et al., *IEEE Trans. Appl. Supercond.* **26** (2016)

G. Celentano et al., *IEEE Trans. Appl. Supercond.* **29** (2019)

ENEA HTS Cable – historical overview



Twisted Al core
6 ducts 4.3x4.3 mm²



35 kA – class cable
(4.2 K - 18 T)

490 mm² cross section

Al core: $\varnothing = 22$ mm
Al or SS jacket: $t = 1.5$ mm

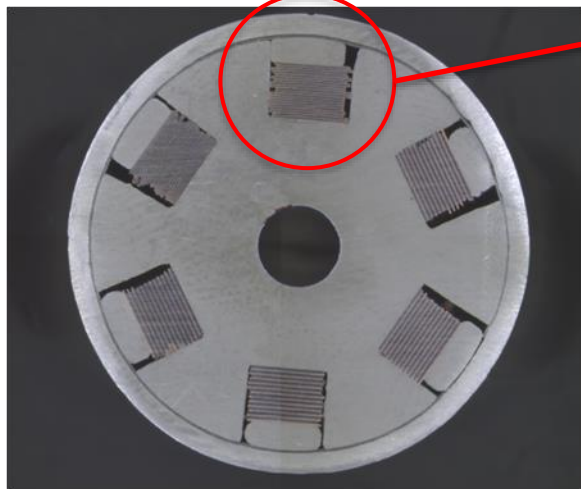
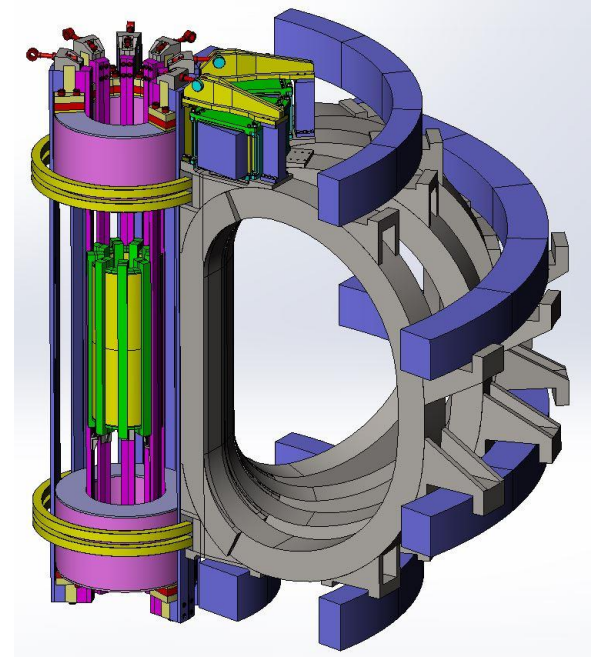
$$J_e \approx 70 \text{ A/mm}^2$$



additional HTS insert
in DTT CS magnet

13.6 T current design (LTS)
18.7 T with HTS insert

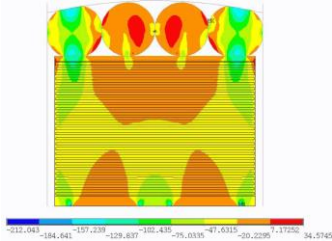
DTT Divertor Tokamak Test



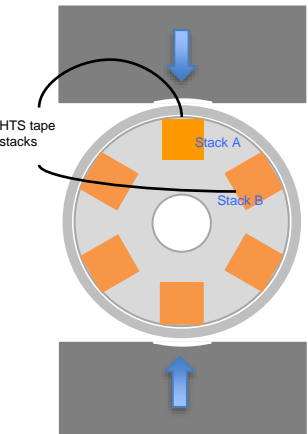
Different duct profile:
no grooves
Different filler:
4x1.5 mm² Al tapes



Reduce
mechanical stress
on tapes



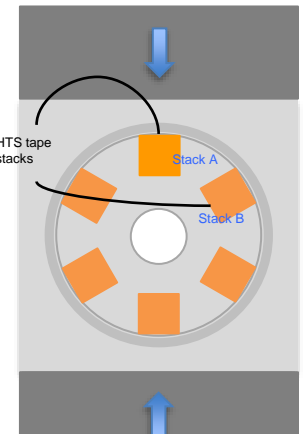
ENEA HTS Cable – historical overview



6-slots

4 dummy slots
(12 SS tapes + 12 Cu tapes)

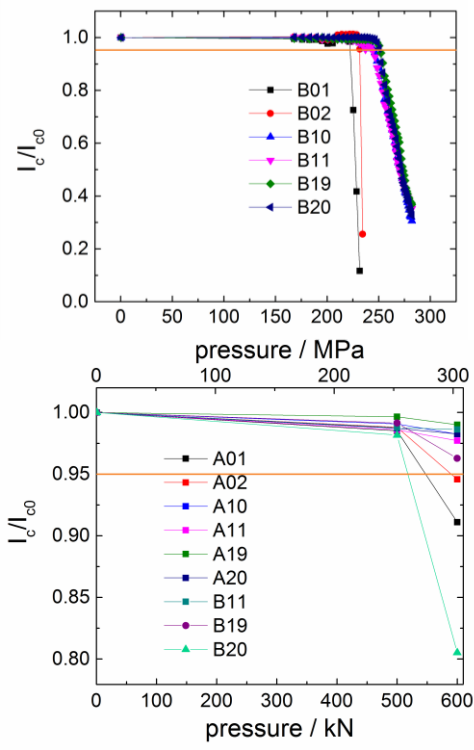
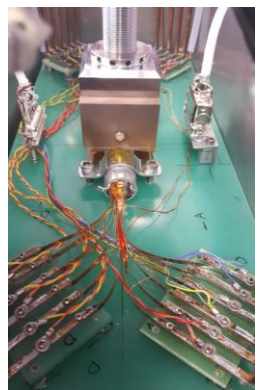
2 fully HTS slots
(20 SuNAM)



stack **A**: compres.
stack **B**: shear

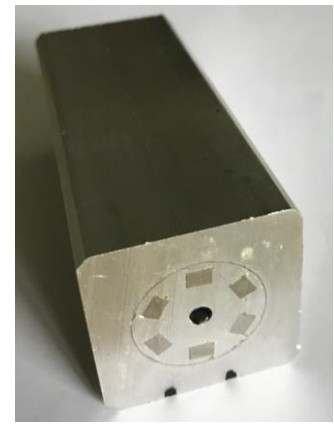
6 tapes per slot
measured at LN₂

max available
force **600 kN**



Round cable
degradation:
> 220 MPa

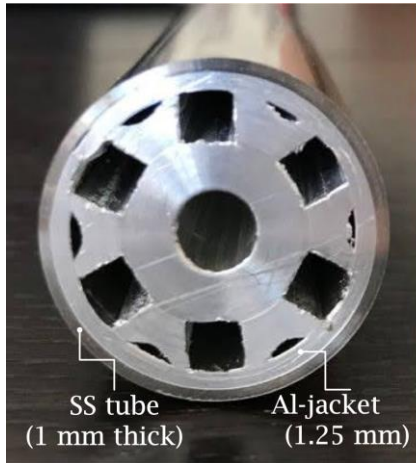
Square cable
degradation
@ 250 Mpa
< 3%



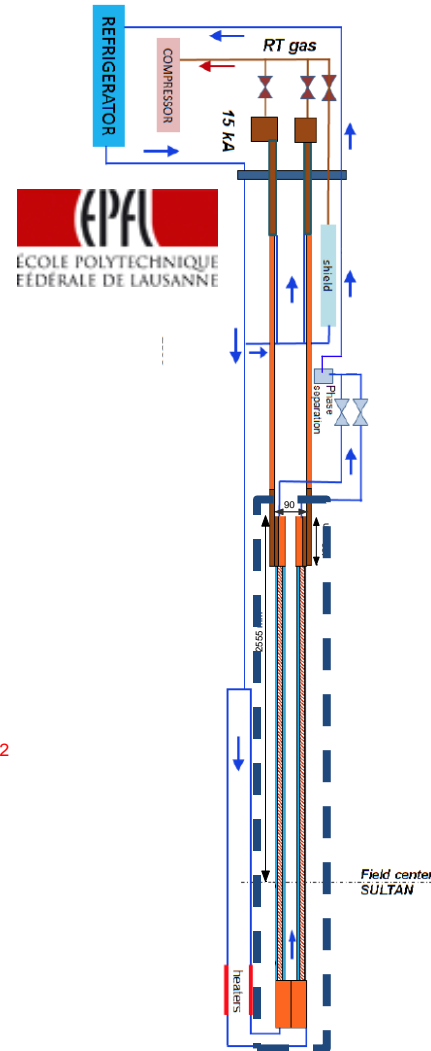
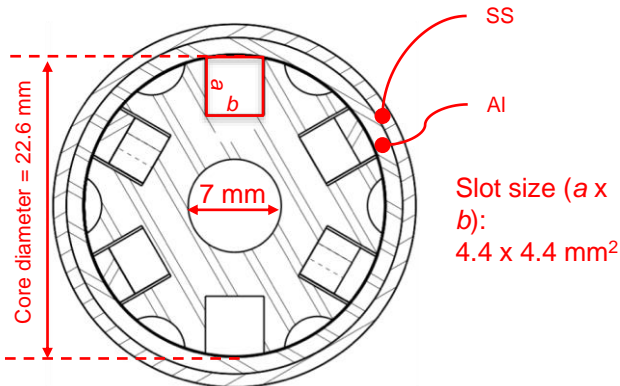
DTT compatible!



ENEA HTS Cable – historical overview

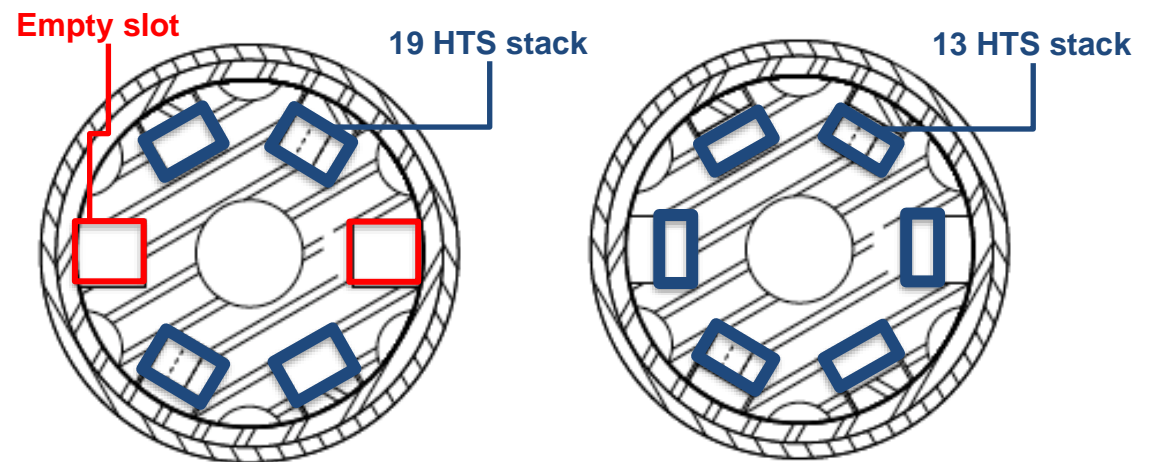


SS tube (1 mm thick) Al-jacket (1.25 mm)



Test at SULTAN facility: 15 kA D.C. current source; forced flow **She** cooling; Max field 11 T

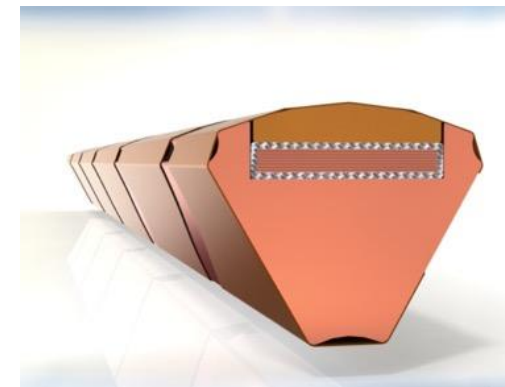
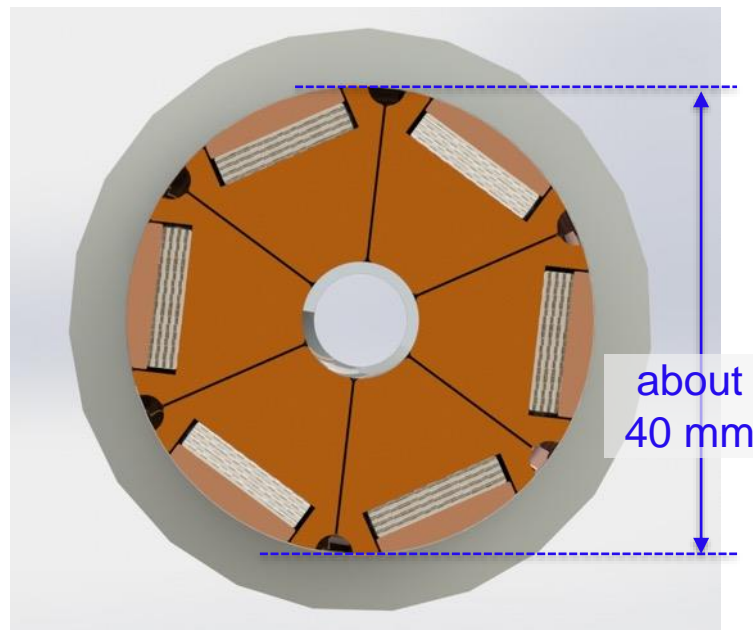
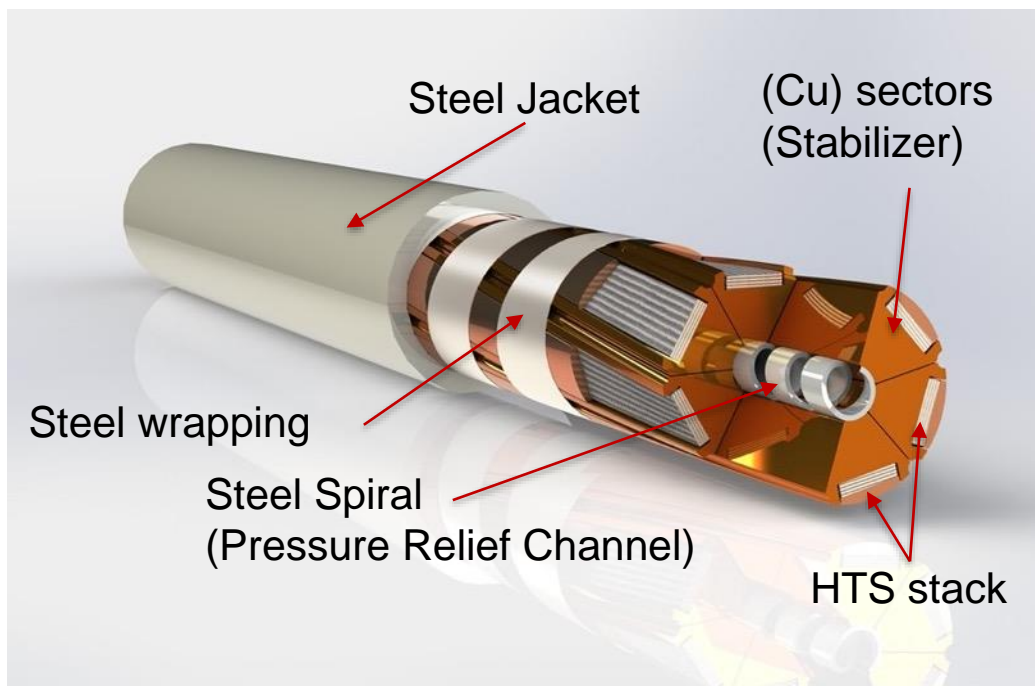
Sample for quench experiment consists of **two conductors (legs)** connected at the bottom through a **joint**
(Mechanical support structure designed to sustain e.m. loads)



November 2023??

ENEA HTS Cable – historical overview

New cable concept: SECTor ASsembled (**SECAS**) CICC



Multi-Stage Cable Processing (easier manufacture)

Lower a.c. losses (non-monolithic structure)

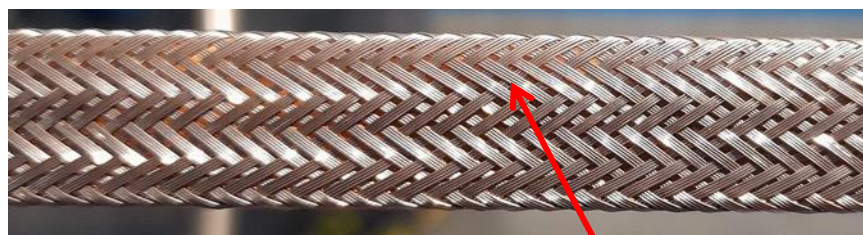
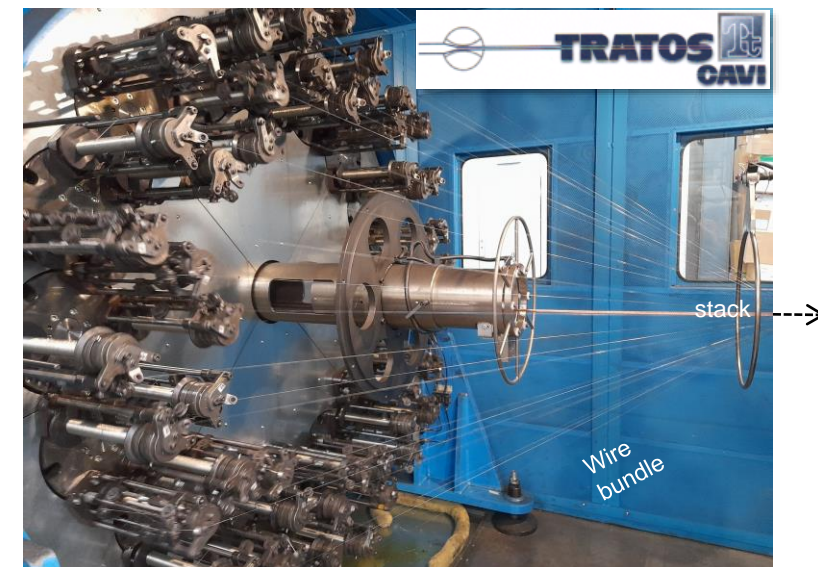
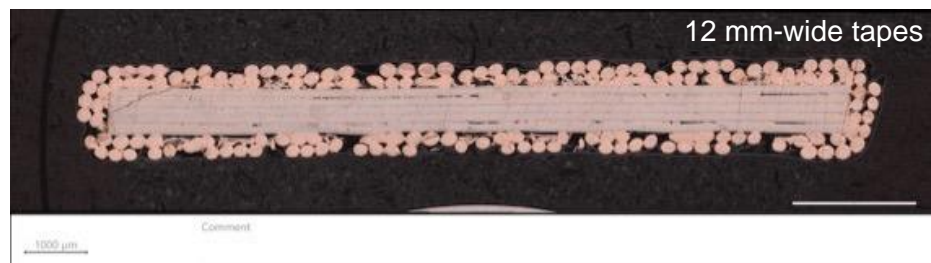
L. Muzzi *et al.*, *IEEE Trans. Appl. Supercond.* **33** (2023)

60 kA – 18 T – 4.5 K – pulsed operation
capable to sustain bending over 1.5 m radius

ENEA HTS Cable – historical overview

New stack concept: BRAided STack (**BRAST**)

Tape stack assembled into a **Cu wire braid**



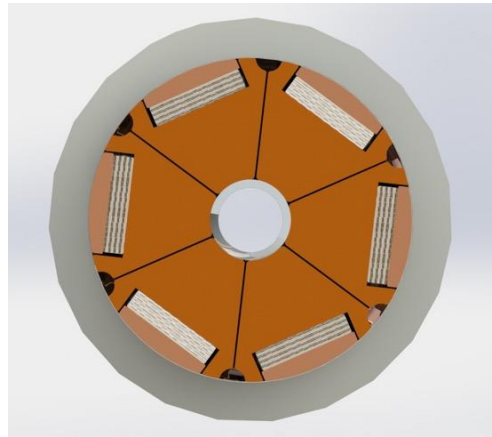
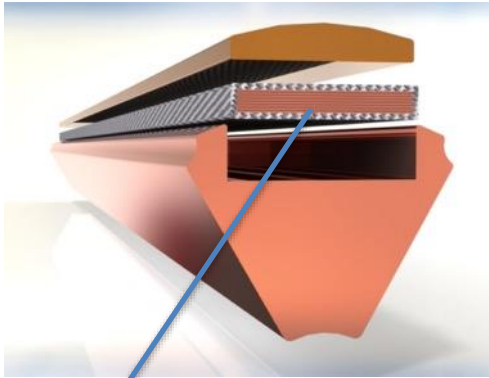
Tin-coated Cu wires
(with diameter between
0.10 mm and 0.3 mm)

Main Features

- extremely effective and easy **processing step** to build a (non-twisted) stack
- protection of the stack it during all successive handling steps
- **flexible** and easy-to-handle cable **sub-unit**

ENEA HTS Cable – historical overview

SECAS + BRAST



3 options

#10 tapes - 12 mm wide



2 x #5 tapes - 12 mm wide



6 x 5 tapes - 4 mm wide

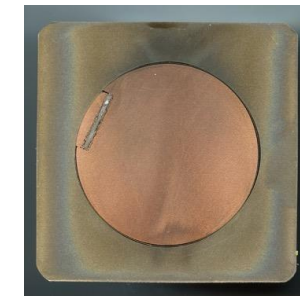
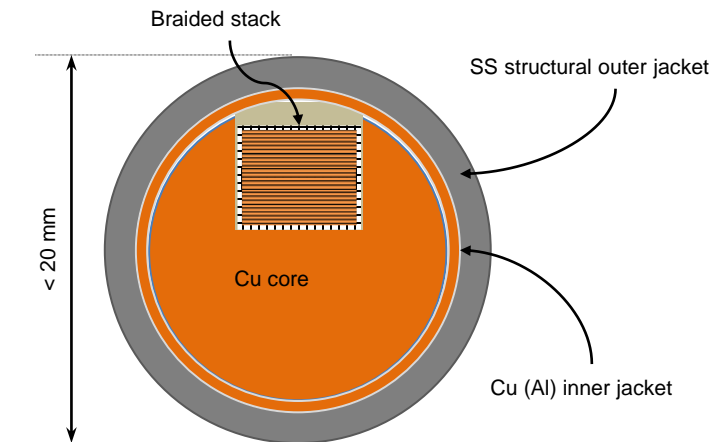


End of 2023

sub-size samples to be tested at **FBI facility (KIT)**
(Force 100 kN, current 10 kA, field 12 T, LHe)

2 Samples:
braided stack with 15 tapes
soldered stack with 15 tapes

Target **5/6 kA @ 4.2 K, 12 T**

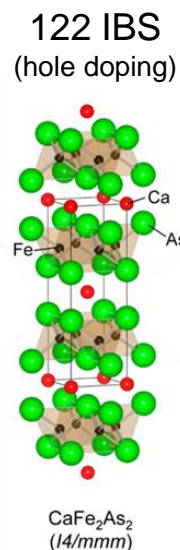
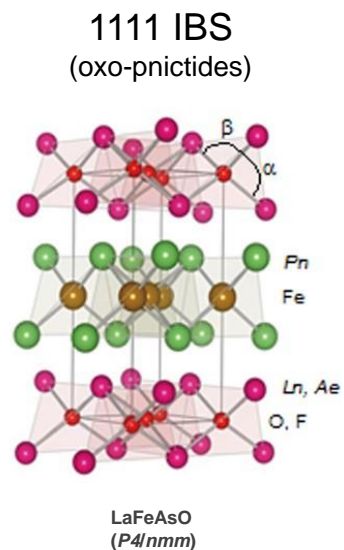


IBS Materials

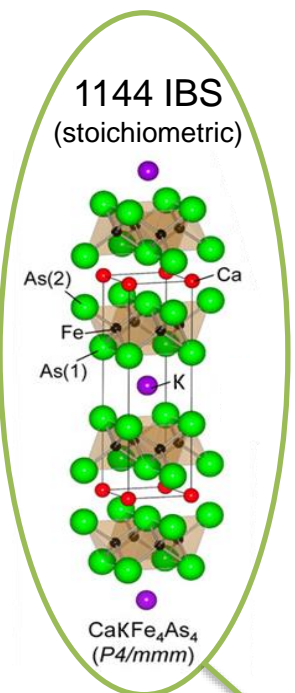
- 11-coated conductors
- 1144 PIT wires

Iron Based Materials

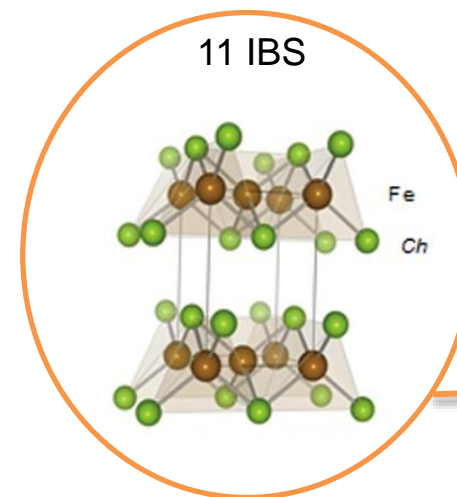
Pnictides



Different ionic radius AE
 substitution



Chalcogenides



Simplified Coated-Conductor technology

- Milder deposition conditions
- Simpler buffer architectures
- Lower sensitivity to bi-axial texture

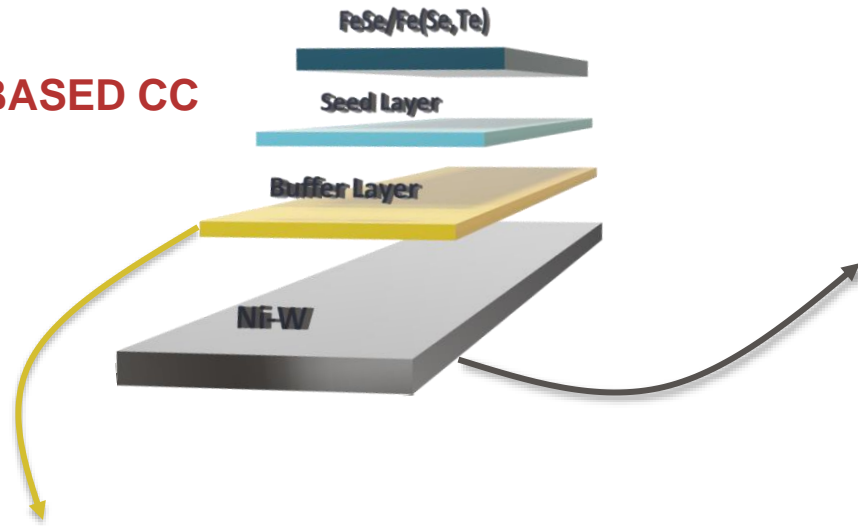
High pinning and H_{c2} values expected
 Suitable for PIT wires manufacturing process

Ae: Ca, Sr, Ba, K, ...
 A: Li, Na, K, Rb, ...
 Pn: As, P
 Ch: Se, Te
 Ln: La, Ce, ...

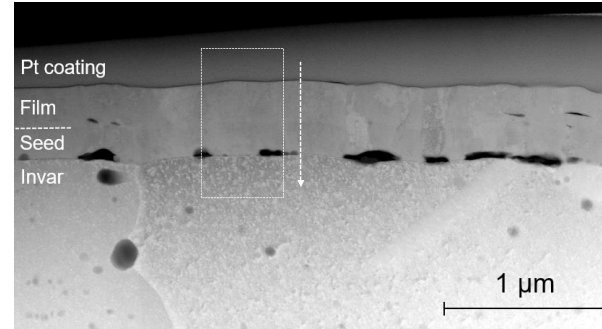
H. Hosono, et al., *Sci. Technol. Adv. Mat.*, **16** (2015) DOI: [10.1088/1468-6996/16/3/033503](https://doi.org/10.1088/1468-6996/16/3/033503)
 A. Iyo et al., *J. Am. Chem. Soc.* **138** 3410–3415 (2016) DOI: [10.1021/jacs.5b12571](https://doi.org/10.1021/jacs.5b12571)
 F.-C. Hsu et al., *Proc. Natl Acad. Sci. USA* **105**,14262 (2008). DOI: [10.1073/pnas.0807325105](https://doi.org/10.1073/pnas.0807325105)
 Q. Si, R. Yu, E. Abrahams, *Nat. Rev. Mater.* **1**, 16017 (2016). DOI: [10.1038/natrevmats.2016.17](https://doi.org/10.1038/natrevmats.2016.17)

IBS-CCs: FeSe/Fe(Se,Te)

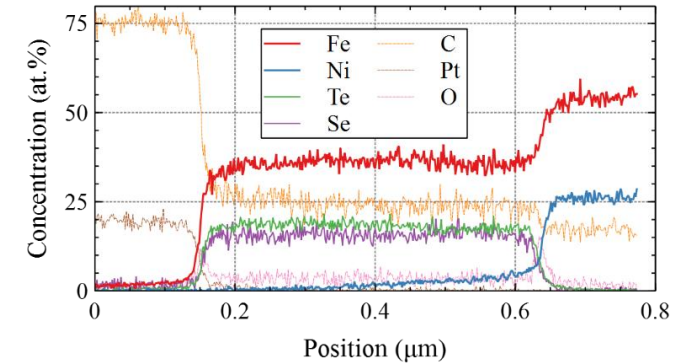
Fe-BASED CC



Fe(Se, Te) on INVAR with or w/o seed layer

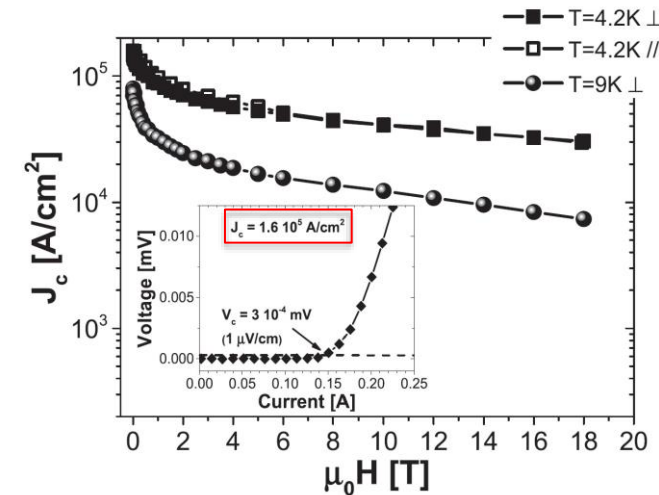
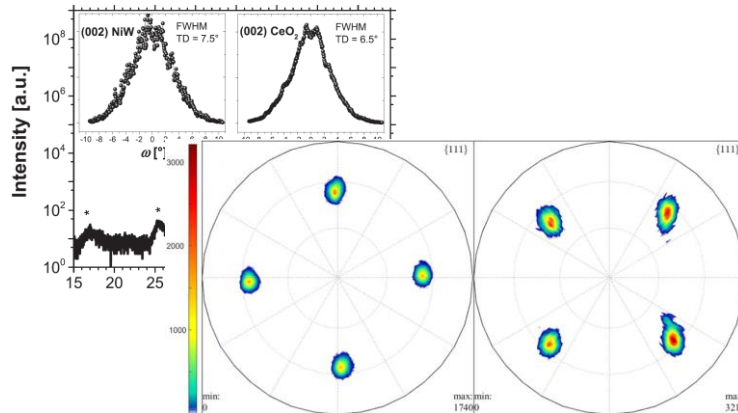
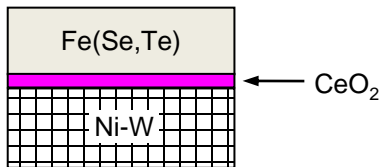


G. Sylva et al., *IEEE Trans. Appl. Supercond.* **29** (2019)



Buffer layer required!

PLD Fe(Se, Te) on PLD CeO₂(350 nm)/NiW



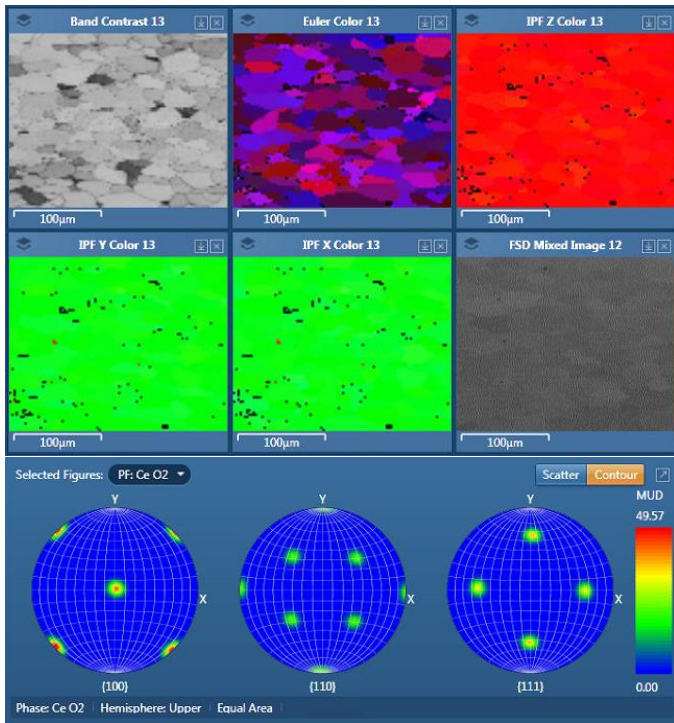
Promising Results

G. Sylva et al., *Supercon. Sci. Technol* **32** (2019)

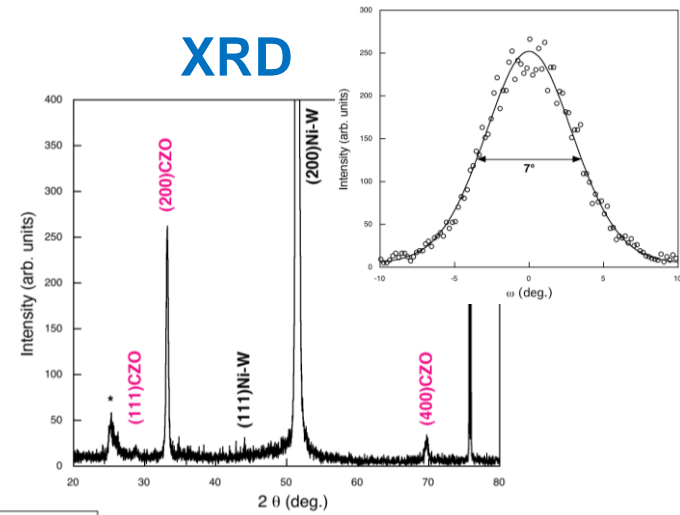
IBS-CCs: FeSe/Fe(Se,Te)

PLD Fe(Se,Te) on MOD Zr-CeO₂(30 nm)/NiW

- Propionate precursor solution of Zr-doped (5%) CeO₂
- Deposition by spin coating on Ni-W (5%) by evico GmbH
- Thermal treatment for precursor solution conversion at 1100 °C for 15 min in flowing Ar-H₂

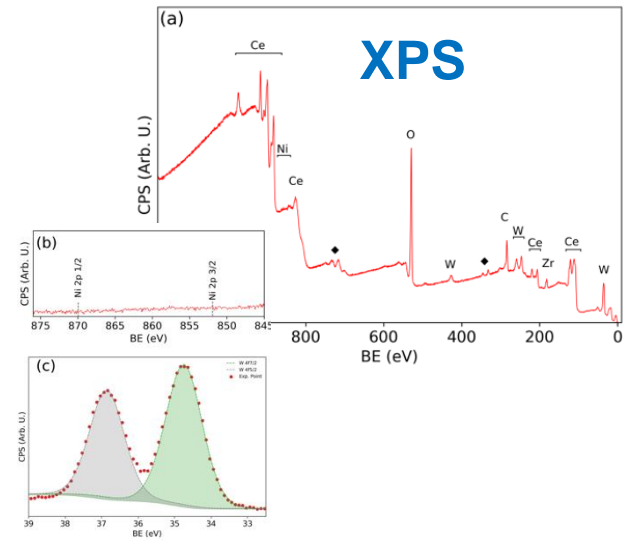


EBSD

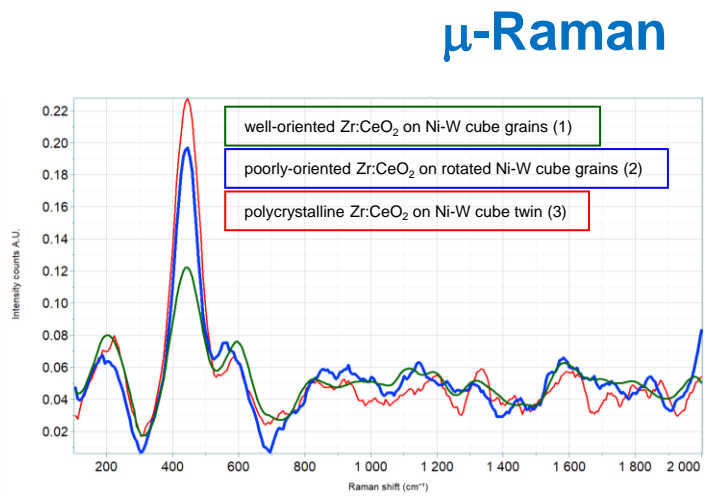


Perfectly suitable
(only 30 nm)

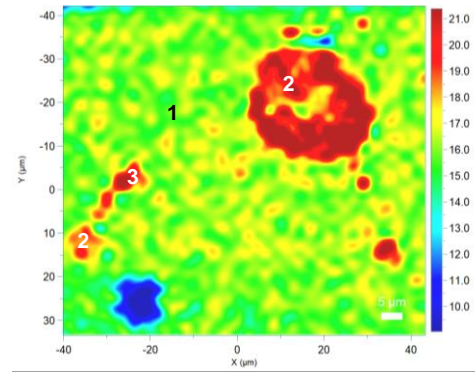
A. Vannozi et al., under review (2023)



XPS

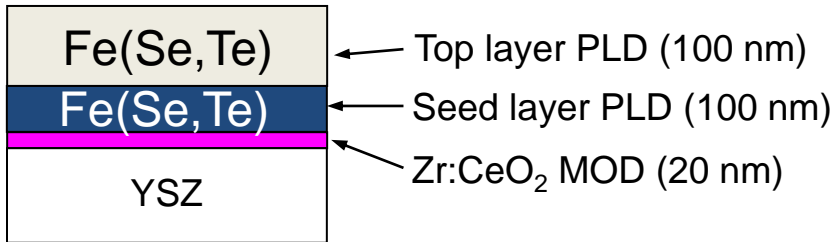


μ-Raman

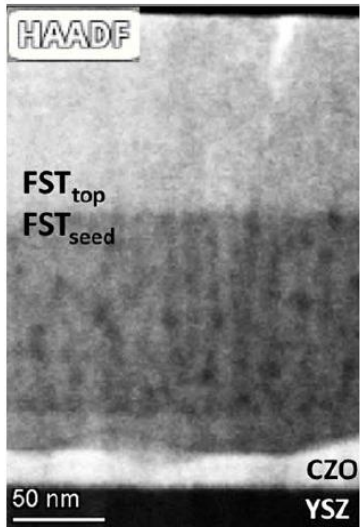
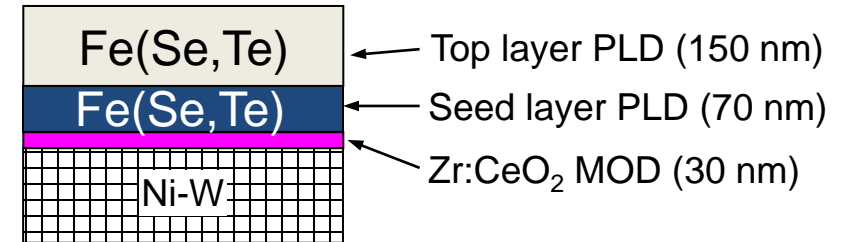


IBS-CCs: FeSe/Fe(Se,Te)

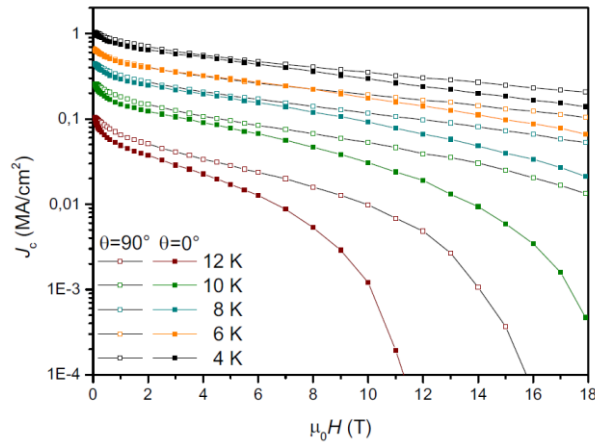
First test: single crystal



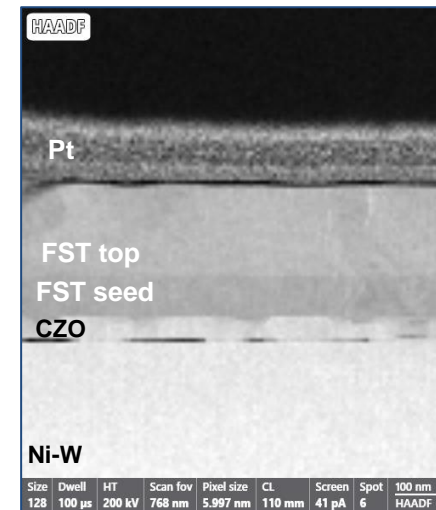
Final step: metallic substrate



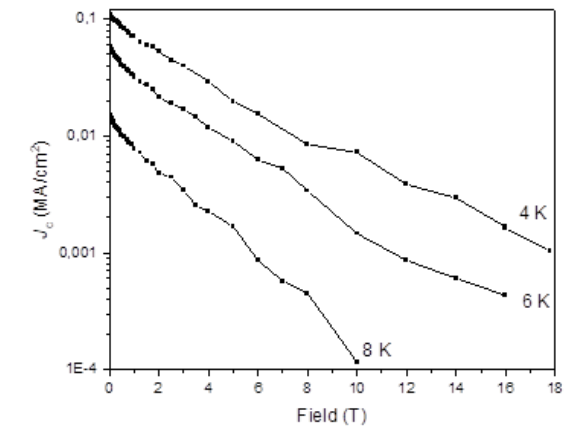
L. Piperno *et al.*, *Sci. Rep.* **13** (2023)



Very good results!



L. Piperno *et al.*, *in preparation*



Lower transport properties

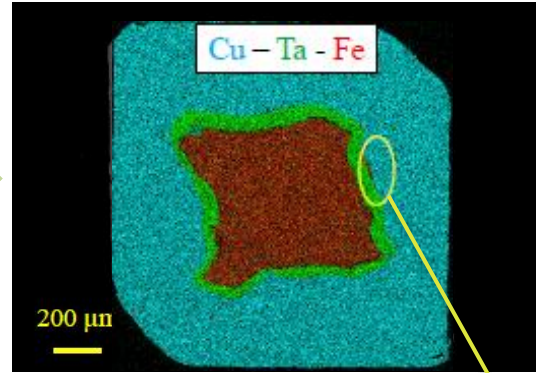
Results in line with PLD-buffer

IBS Materials

- 11-coated conductors
- 1144 PIT wires

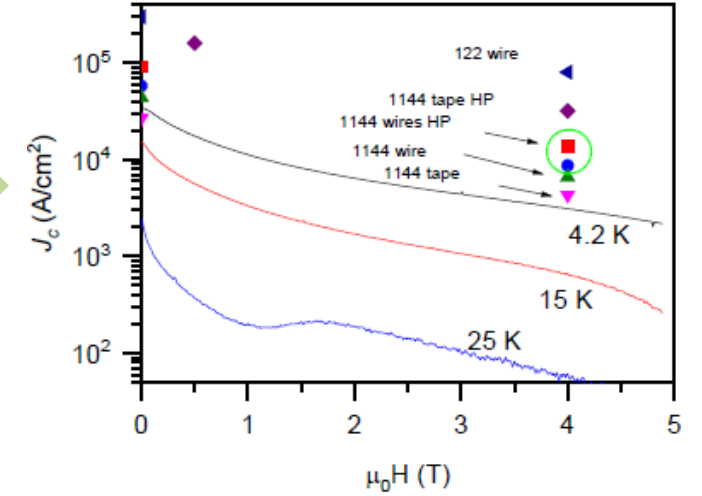
1144-IBS PIT wires

PIT process: powder insert + groove rolling + thermal treatment



Some powder out of the barrier during insertion

A.Masi et al., Superconductivity 2 (2022) 100014



Promising results

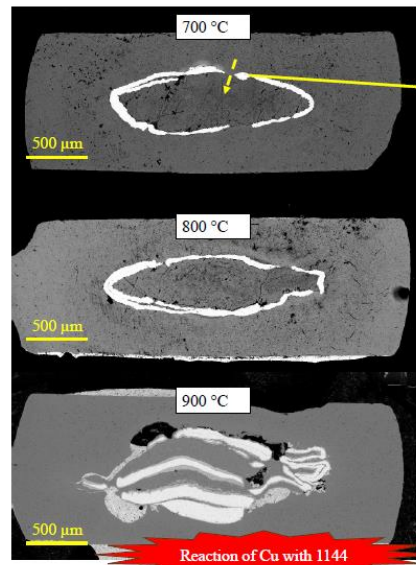
Possible enhancements:

HiP process (densification)

Lamination (improves texturing)

A.Masi et al., Under review

Deformation issues on Ta sheet



Ongoing activity

FUNDED



CfP-FSD-AWP24-ENR-04-ENEA-03



Conclusions

The ENEA HTS group is mainly focused on Coated-Conductors in all its aspects, from material optimisation to applications.

The use of different deposition techniques allows us to study all the layers that make up a coated-conductor, while our combined expertise with the LTS group allows us to study the application of tapes in high field magnet cables

About IBS materials, our tape expertise was applied to the search for a simplified process for Fe(Se,Te) coated-conductors.

1144 material, with great potential in PIT wire applications, is also being studied showing very promising results

We are proudly the best in another wire manufacturing process



Fig. 1 - Left panel: Spaghetti wires (cold extruded) “alla amatriciana” (tomatoes, pig cheek lard, pecorino cheese, EV olive oil); Right panel: equipment used for the spaghetti wires manufacturing process

Open to collaborations on this topic

Thanks for your



Thanks for your

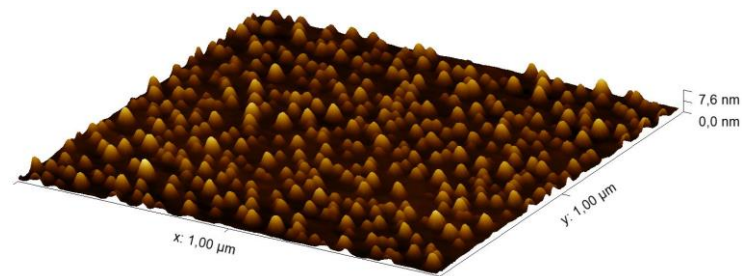
85 At Astatine (209.9871)	52 Te Tellurium 127.60	7 N Nitrogen 14.0067	22 Ti Titanium 47.867	8 O Oxygen 15.9994	7 N Nitrogen 14.0067
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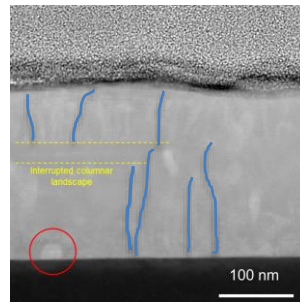
Film nano-engineering (APC) – additional slide

Modified template

MOD ZrO₂ nanoislands

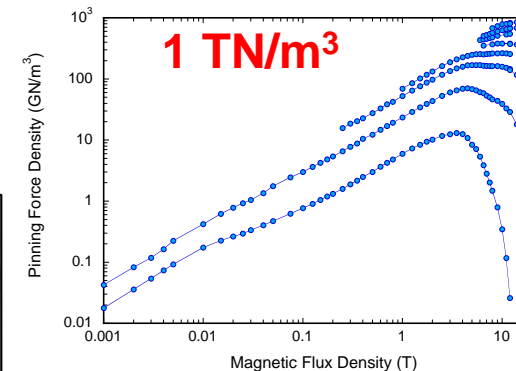
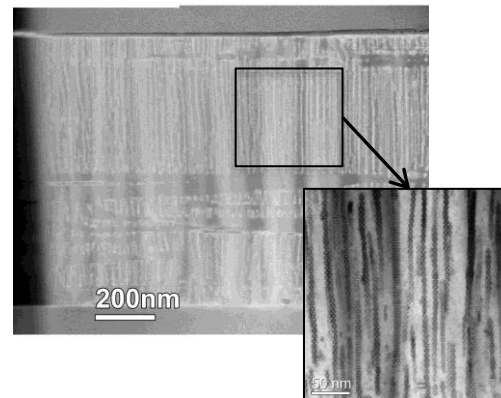


L. Piperno et al., *Appl. Surf. Sci.* **484** (2019)

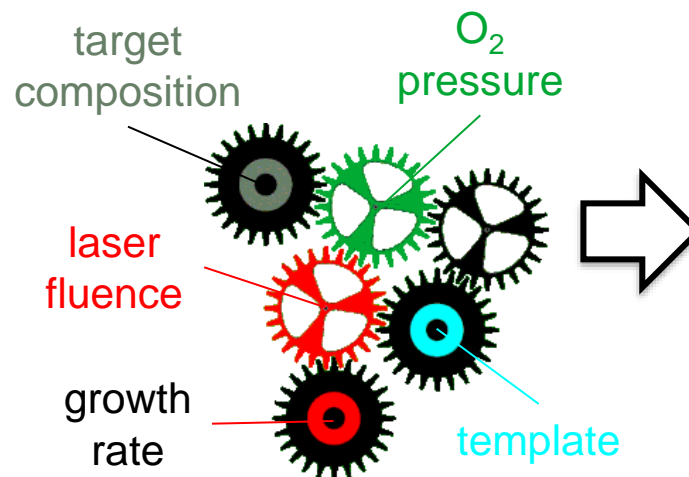


F. Rizzo, *in preparation*

Results replicated on Thick films (~ 1 μm)

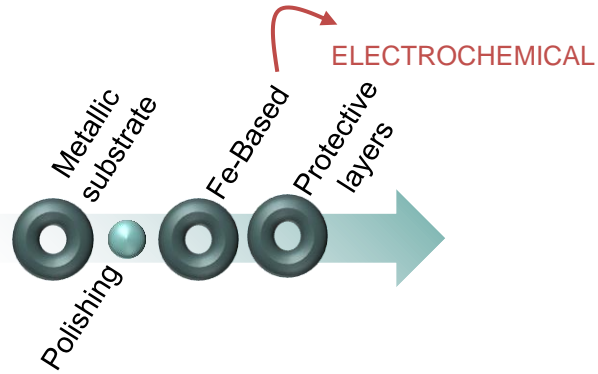


Deep knowledge on
BYNTO/YBCO system

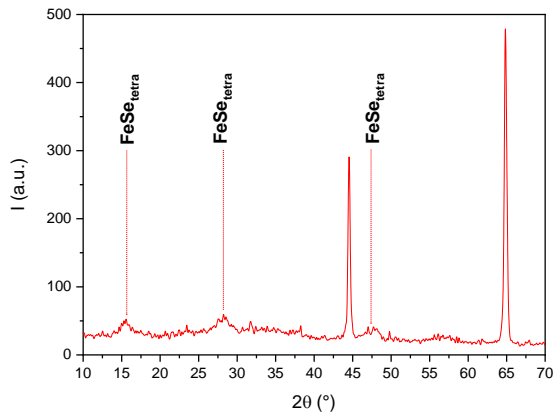
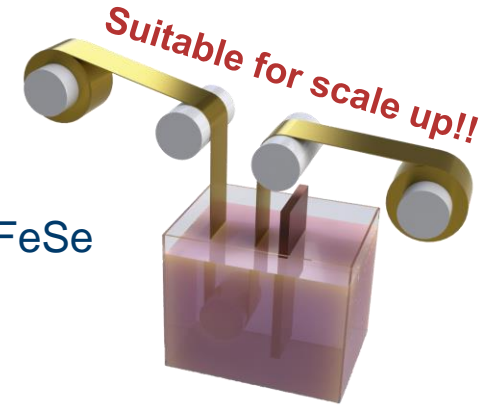


Optimization in specific
operational regimes (T , B)
for different applications

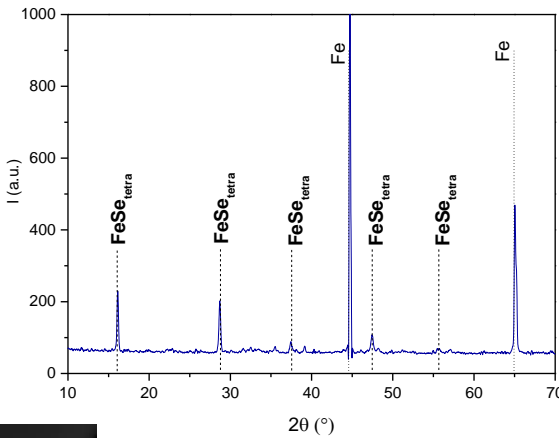
Process simplification for IBS-CCs additional slide



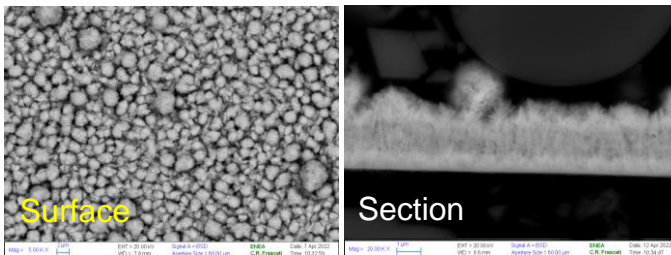
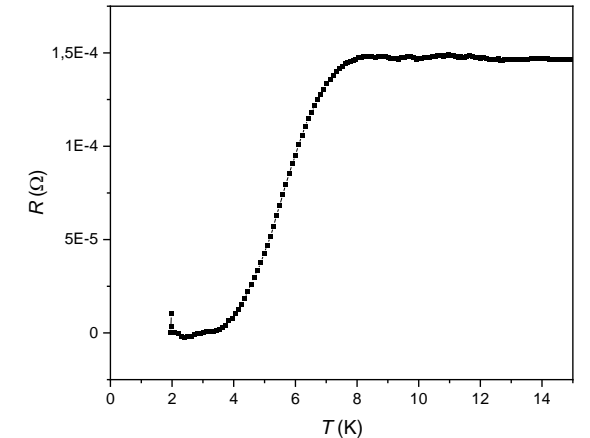
MATERIAL: FeSe
TECHNIQUE: Electrodeposition
RESULTS: - Formation of FeSe_{tetra}
 - Induced superconductivity in electrochemical FeSe



RESERVED



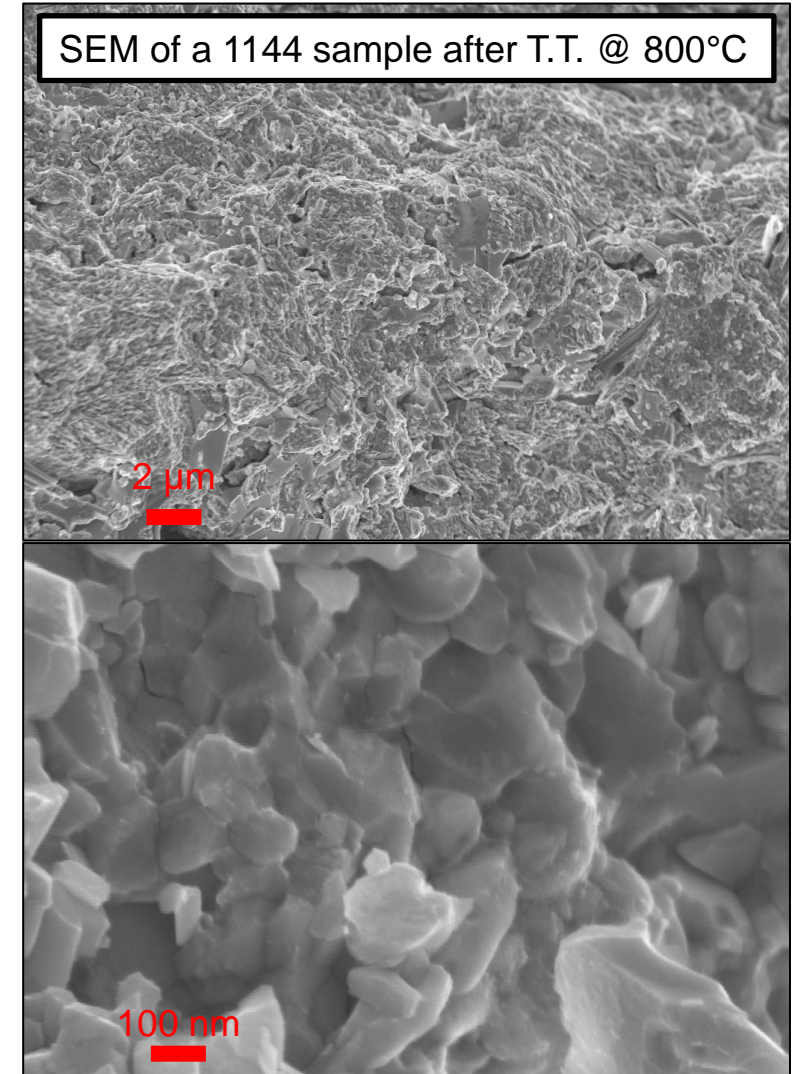
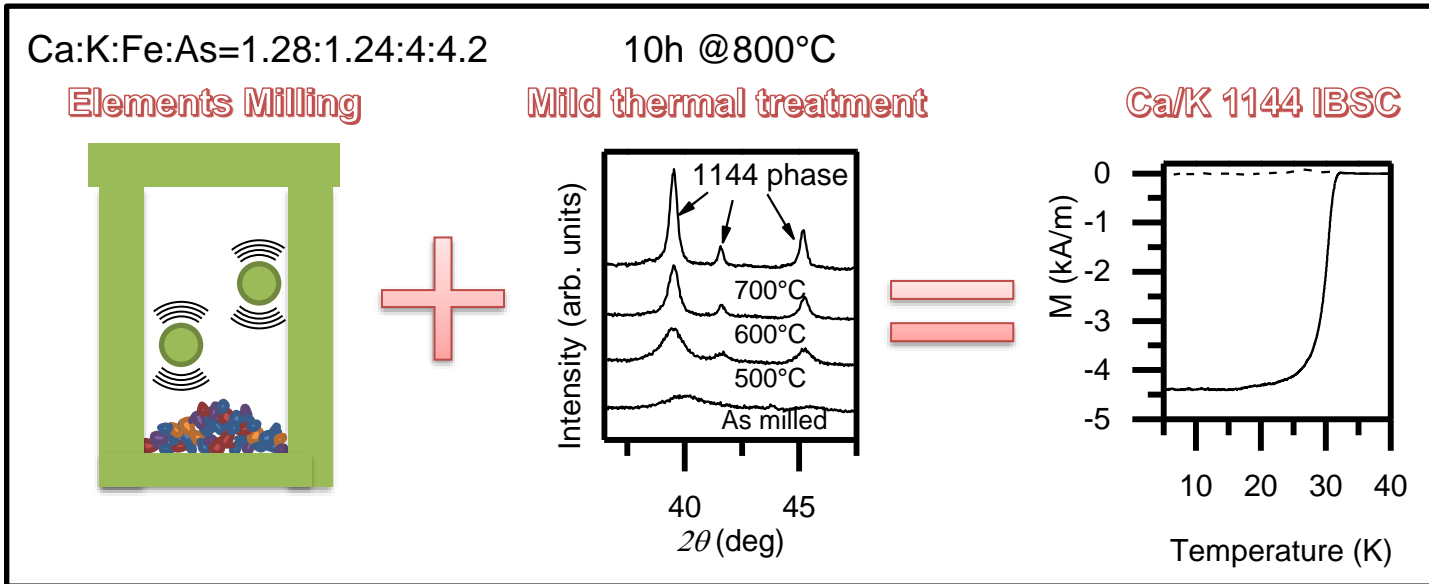
RESERVED



Activity still ongoing – challenging but promising

1144-IBS – additional slide

Mechano-chemical synthesis of $\text{CaKFe}_4\text{As}_4$ (1144)



Polycrystalline Samples

Structure similar to 122



PIT process

High potentiality in Wire Applications

S.Pyon et al, Appl. Phys. Express (2018)
Z.Cheng et al, Supercond. Sci. Technol. (2019)

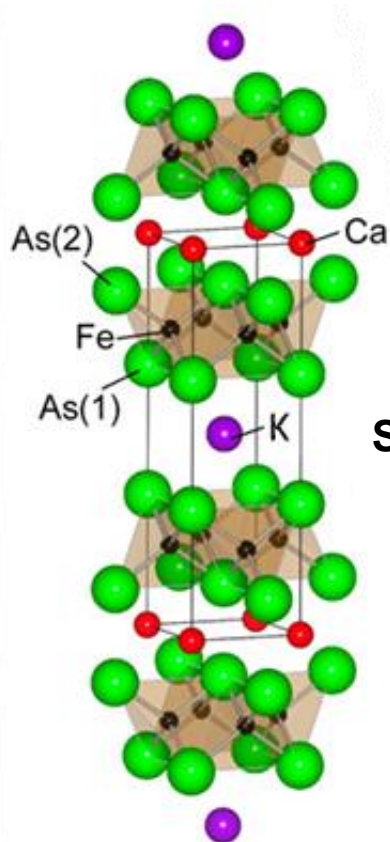
1144-IBS with aliovalent doping – additional slide

Aliovalent substitution:

different valence (alkaline <-> alkaline earth) – similar ionic radius



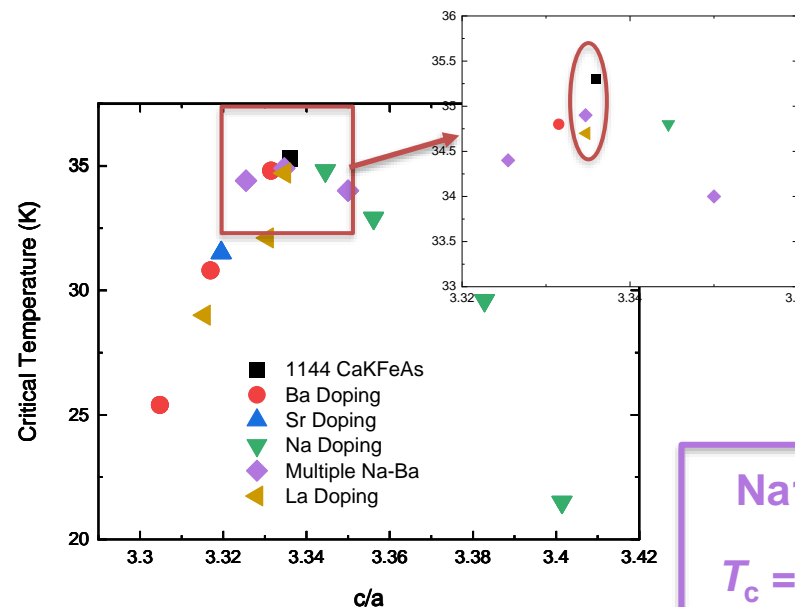
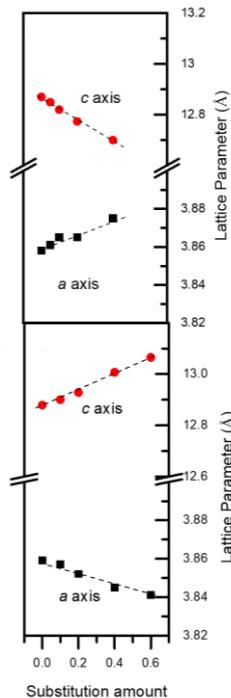
Increased entropy
Influence on Pinning and/or GB



Ba replacing K

Simultaneous doping

Na replacing Ca



A. Masi *et al.*, *Supercond. Sci. Technol.* (2022)

A. Duchenko *et al.*, *under review* (2023)

1144

$T_c = 34.7$ K

Na1Ba05

$T_c = 34.6$ K

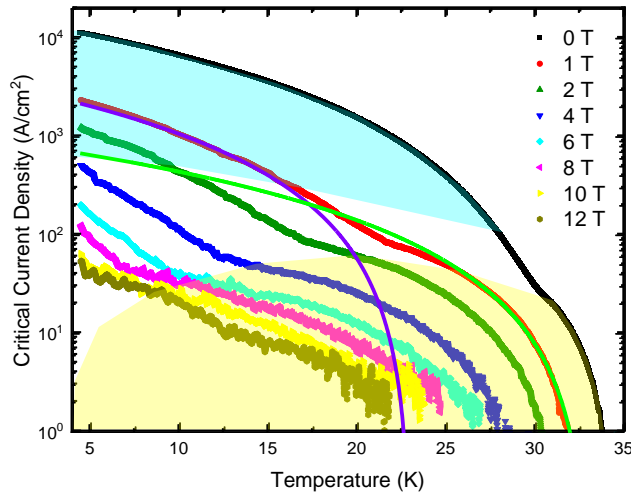
La05

$T_c = 33.4$ K

1144-IBS with aliovalent doping – additional slide

Detailed magnetic characterizations

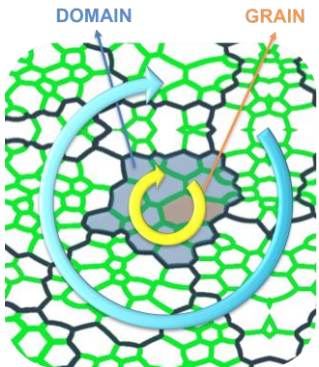
(magnetization, magnetic relaxation, a.c. susceptibility)



Transport properties are still **GB limited** (10^7 A/cm² in s.c.)



Huge room for improvements



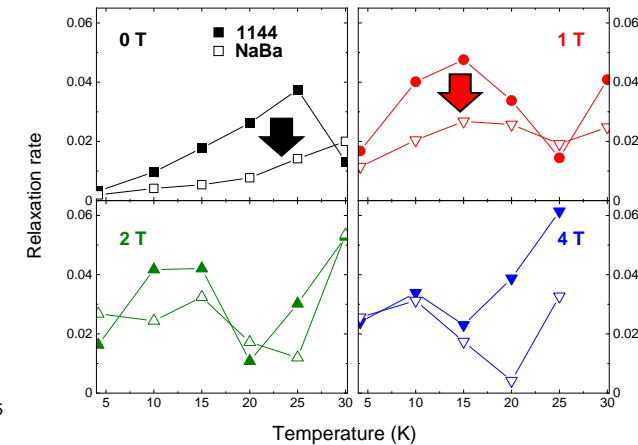
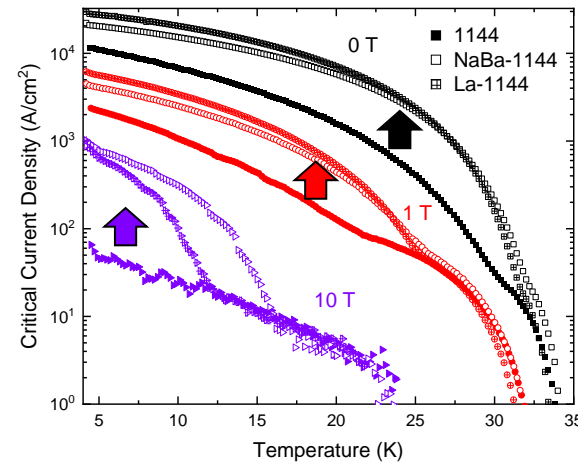
2 contributions:

- Domain boundaries (active at LFT)
- Grain boundaries (active at HFT)

A. Augieri et al., *IEEE Trans. Appl. Supercond.* **33** (2023)

A. Augieri et al., *Under Review*

Effect of aliovalent doping



s.f. J_c more than doubled

Magnetic properties improved in the LFT regime

Aliovalent doping influences the Domain Boundaries properties

Right path but further efforts required