Joining Ion Transport Membranes Using A Novel Transient Liquid Phase Method

Darryl P. Butt
Boise State University
1910 University Drive
Boise, ID 83712

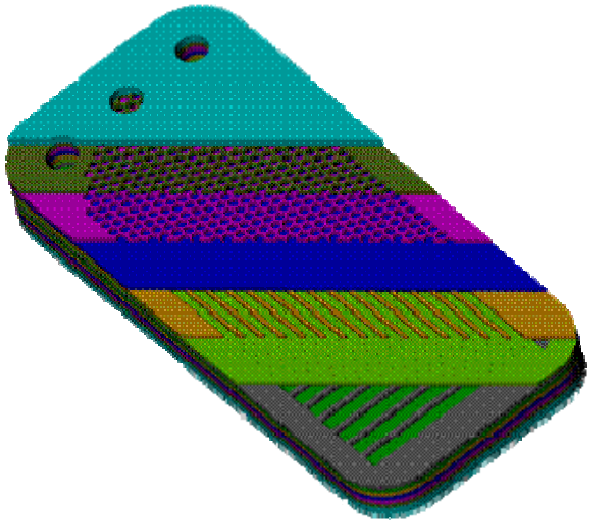


Illustration: M. Wilson, Ceramatec, Inc.

Graduate Assistant: Patrick Callahan, BSU
Industrial Collaborators: Raymond Cutler, Ceramatec, Inc. and Mike Carolan, Air Products and Chemicals

Funding: DOE-Coal, Phase I, 8/31/05-8/30/06
DE-FG26-05NT42536

Contact: Darryl Butt, Professor
darrylbutt@boisestate.edu

Desirable Attributes of Interfaces

Ex.

- Strength
- Hermetic
- Thermal stability
- Chemical compatibility
- Economical
- Pressureless Process
- Simple Process

Contact: Darryl Butt, Professor
darrylbutt@boisestate.edu

Methods of Joining

Ex.

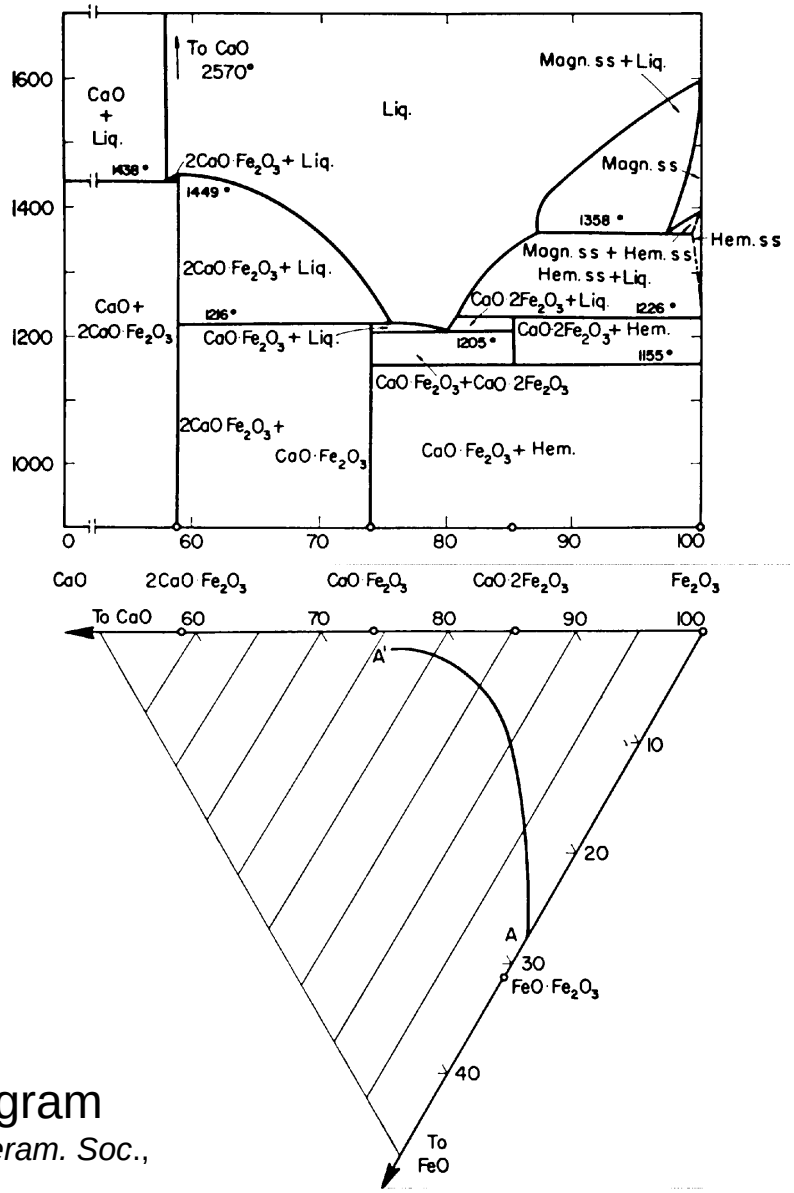
- Metallic Brazes
- Glasses/Ceramic-Glass Composites
- Diffusion Bonding
- Nanocrystalline Interlayers
- Oxide-Metal Eutectics/TLP Metal
- Mechanical Seals

Contact: Darryl Butt, Professor
darrylbutt@boisestate.edu

Example System: $(La_xCa_{x-1})Fe_yO_{3-z}$

Contact: Darryl Butt, Professor
darrylbutt@boisestate.edu

CaO-Fe_2O_3 Binary System



CaO-Fe_2O_3 Phase Diagram

B. Phillips and A. Muan, *J. Am. Ceram. Soc.*, **41** [11] 445-454 (1958).

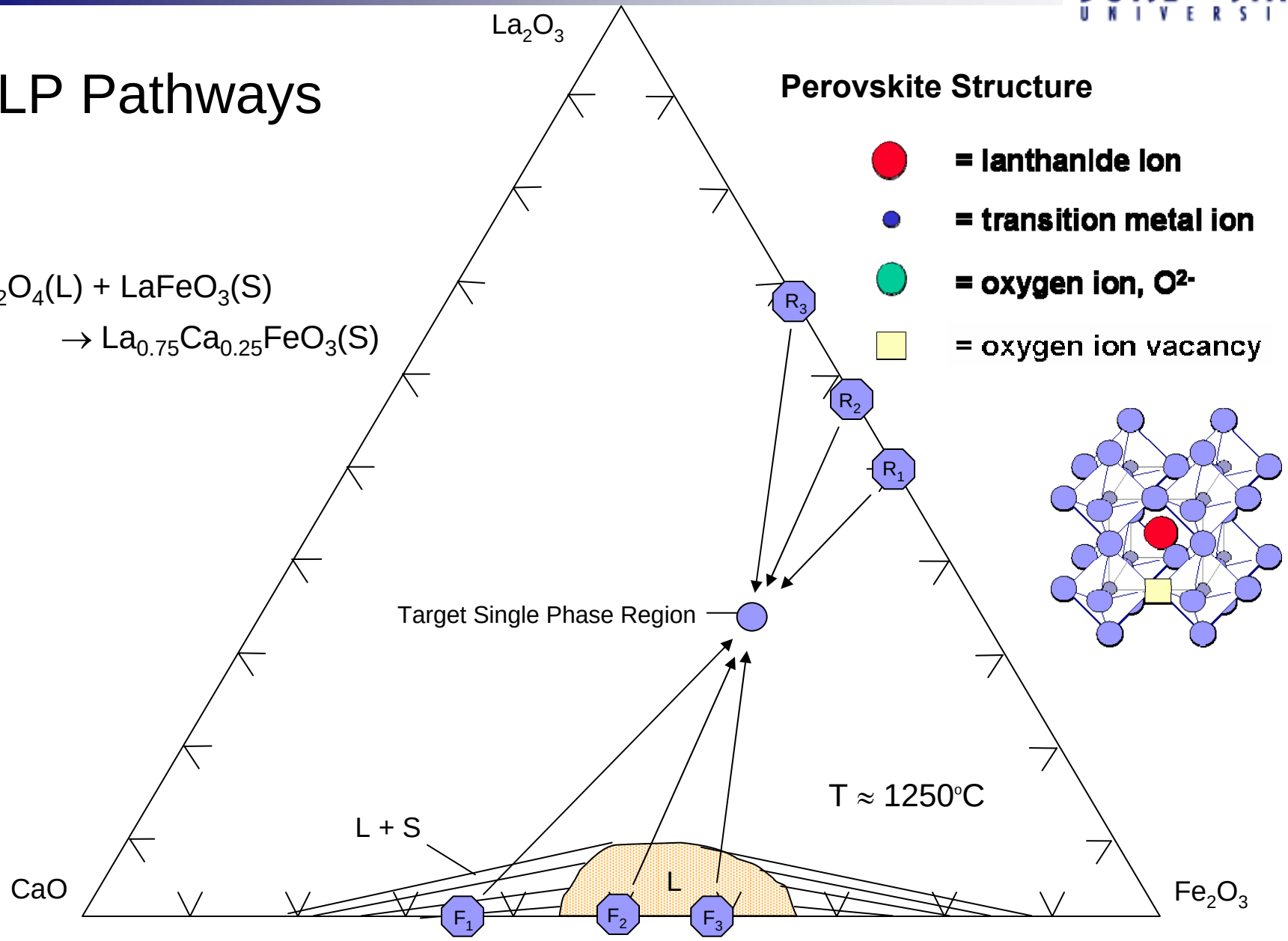
Contact: Darryl Butt, Professor
darrylbutt@boisestate.edu

TLP Pathways

Ex.:

$CaFe_2O_4(L) + LaFeO_3(S)$

$\rightarrow La_{0.75}Ca_{0.25}FeO_3(S)$



Perovskite Structure

= lanthanide ion

= transition metal ion

= oxygen ion, O^{2-}

= oxygen ion vacancy

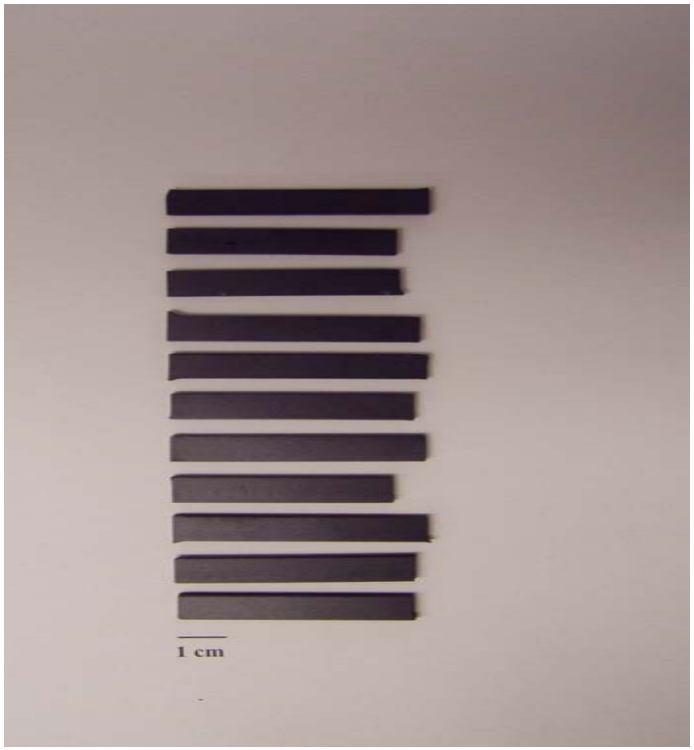
Contact: Darryl Butt, Professor
darrylbutt@boisestate.edu

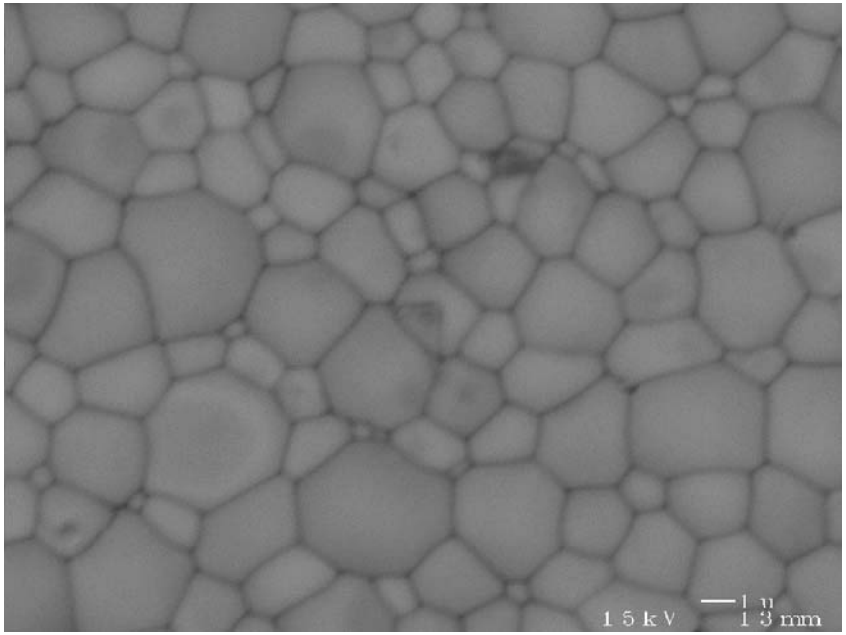
Examples of Other Candidate TLP or PTLP Systems

	System	Pseudo-Binary System	Melting Point
1	SrO-BaO-B2O3	SrO-BaB2O4	920-984
2	SrO-Bi2O3-CaO-CuO-PbO	(Bi,Pb)2Sr2Ca$_{n-1}$Cu$_n$O$_x$	850-863
3	SrO-Bi2O3-CaO-CuO	SrCaBinCu3-nOy	790-845
4	SrO-CaO-V2O5	Ca(VO3)2-Sr(VO3)2	642
5	SrO-CaO-V2O5	Ca2V2O7-Sr2V2O7	980-1060
6	SrO-CuO-La2O3	La2CuO4-Sr2CuO3	1224-1346
7	SrO-MgO-V2O5	Mg(VO3)2-Sr(VO3)2	615
8	SrO-MgO-V2O5	Mg2V2O7-Sr2V2O7	900-925
9	SrO-MoO3-La2O3	SrMoO4-La2(MoO4)3	1005-1112
10	SrO-MoO3-Sm2O3	SrMoO4-Sm2(MoO4)3	1100-1130
11	SrO-Sm2O3-MoO3	SrMoO4-Sm2(MoO4)3	1100-1130
12	Cu2O-CoO-CuO-Co2O3	CoO-CuO	1035-1070
13	Cu2O3-CuO-Al2O3	Al2O3-CuO	1140-1250
14	MnO-SrO-MnO2	SrMnO3-Mn3O4	1415
15	CaO-MnO-SiO2	Ca2SiO4-Mn2SiO4	1240-1375
16	CaO-MnO-GeO2	CaGeO3-MnGeO3	1190-1220
17	CoO-Bi2O3-Fe2O3	Bi2O3-CoFe2O4	760

Contact: Darryl Butt, Professor
darrylbutt@boisestate.edu

$La_{.75-.9}Ca_{.25-.1}FeO_{3-x}$ Microstructure and Joining Specimens for Scoping Studies





Tape Cast and Laminated, Sintered at 1400°C

Contact: Darryl Butt, Professor
darrylbutt@boisestate.edu

Basic Processing Steps

The raw materials, Fe_2O_3, $CaCO_3$, and La_2O_3, are combined

$Fe_2O_3 + CaCO_3 + La_2O_3$

Powders are mixed

Powders are calcined in air at 850°C

Powders are milled in isopropanol in a Retsch PM 100 Ball Mill

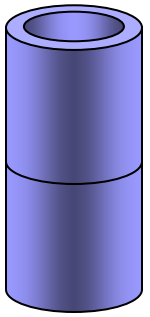
$Fe_2O_3 + CaO + La_2O_3$

Powders are dried and screened through a sieve

An ink or tape is made using the processed powder

Ink or tape is situated between parts to be joined

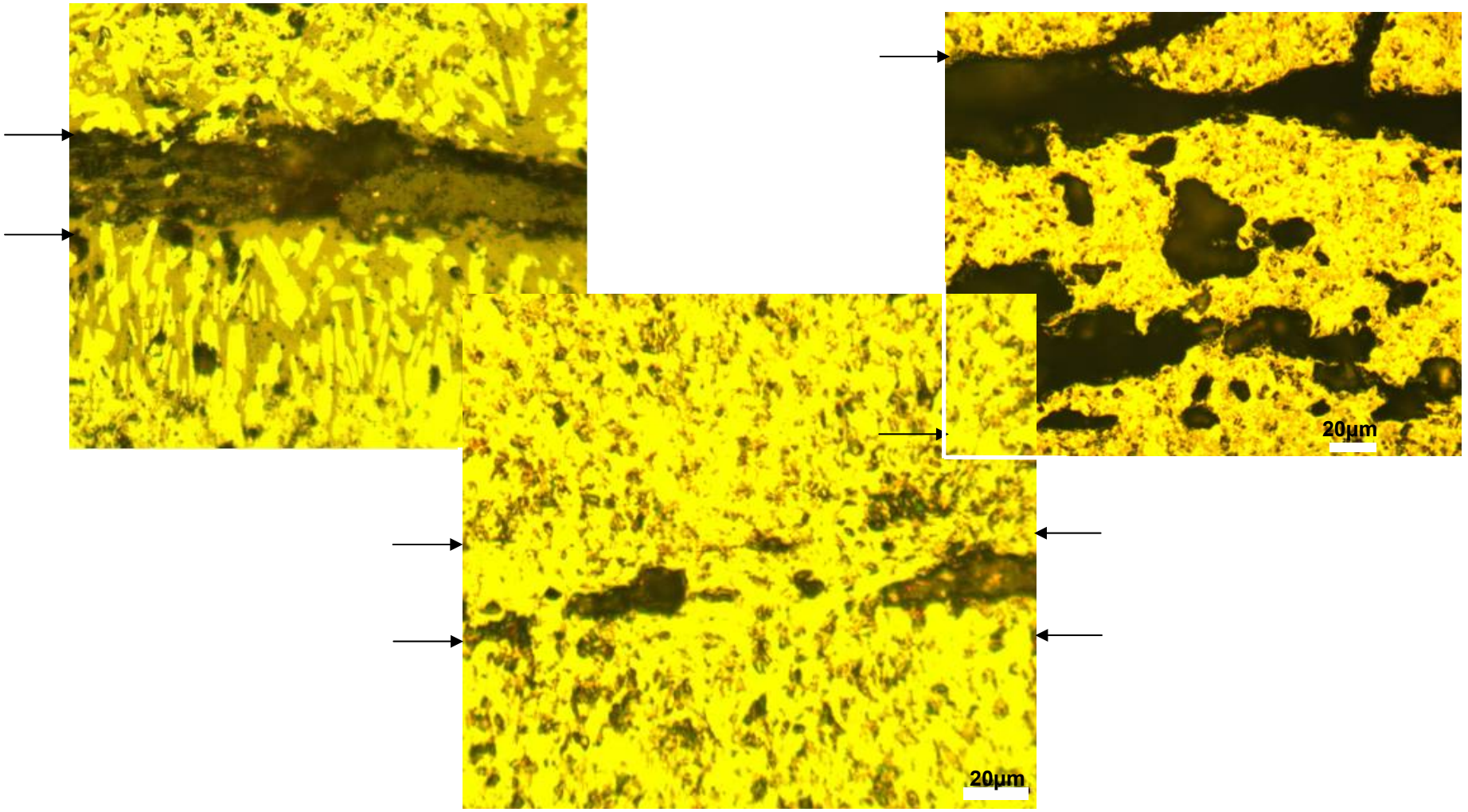
Parts are placed in furnace and heated above the TLP melting point



$La_{0.9}Ca_{0.1}FeO_3$

Contact: Darryl Butt, Professor
darrylbutt@boisestate.edu

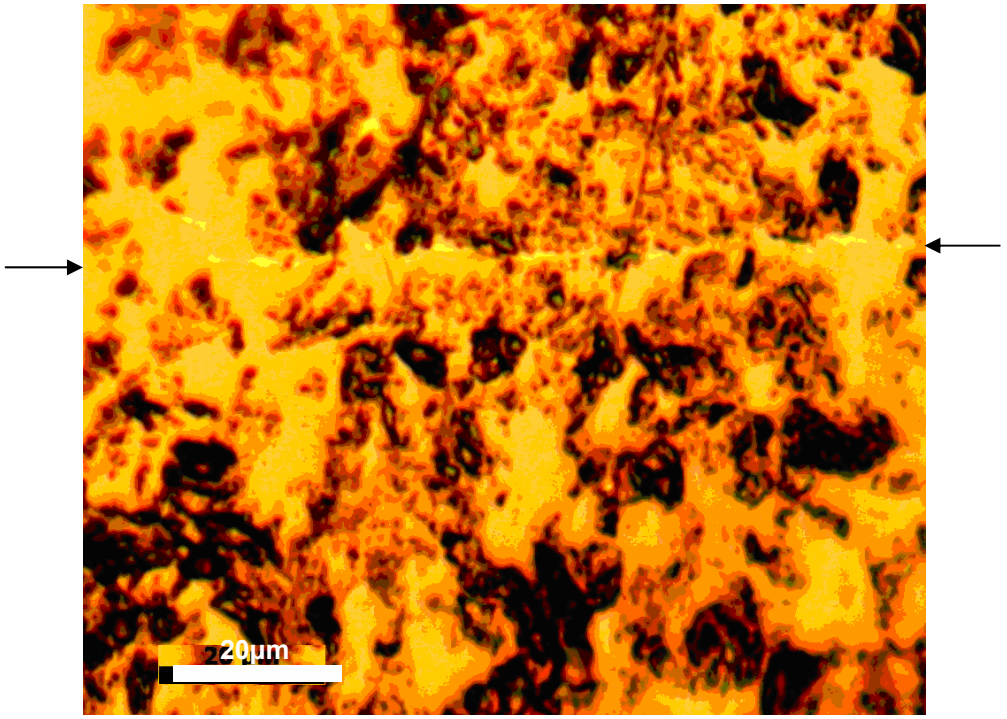
Unsatisfactory Joint Interfaces Fabricated Using Course Powders



Contact: Darryl Butt, Professor
darrylbutt@boisestate.edu

Improved Small Coupon Joint Interface

Virtually no voids present, grain boundary migration

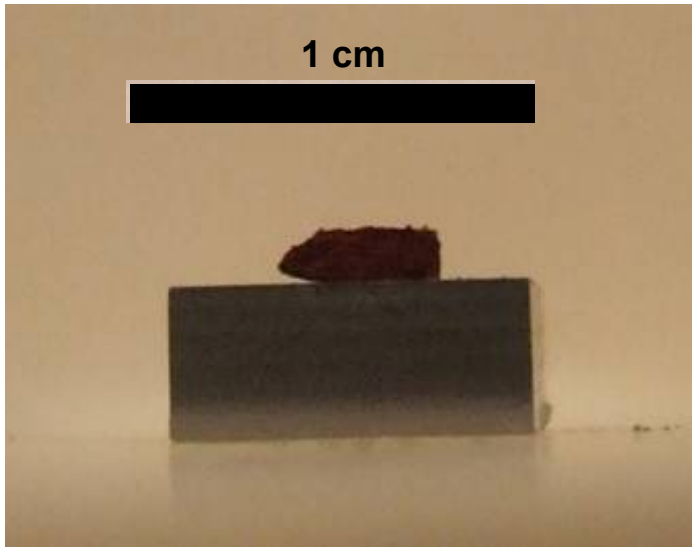


Ink applied by hand, joined at 1400°C for 4hrs

Contact: Darryl Butt, Professor
darrylbutt@boisestate.edu

Wetting of the Ca_xFeO_y Phase

Before heating



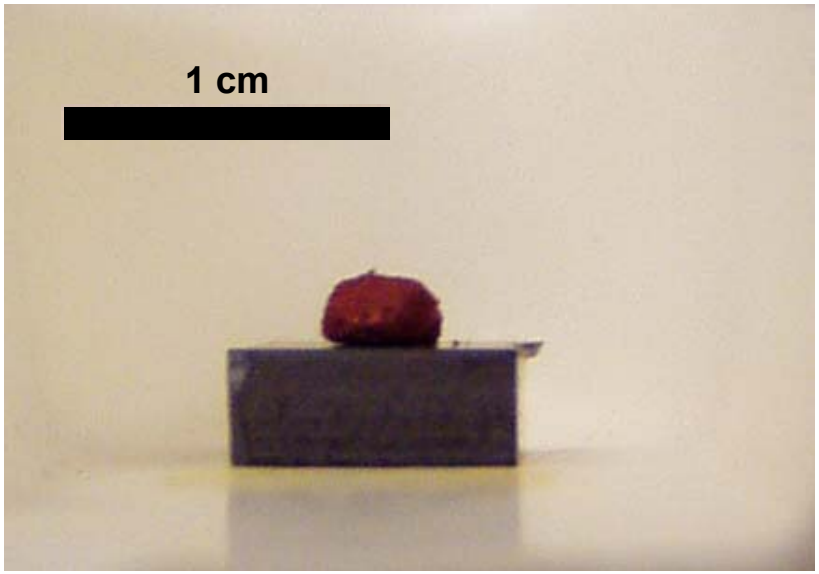
After heating

Wetting angle is immeasurable, and the $La_{0.9}Ca_{0.1}FeO_3$ piece has joined with the alumina boat.

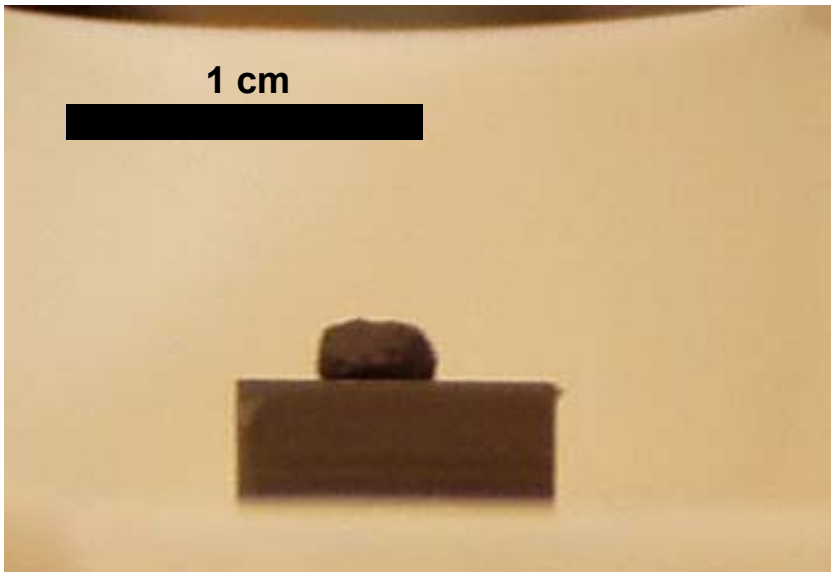
Contact: Darryl Butt, Professor
darrylbutt@boisestate.edu

Wetting vs. Refractory Phase Formation

Two Phase Mixture Can React Rapidly, Forming Refractory Phase Prematurely



Before

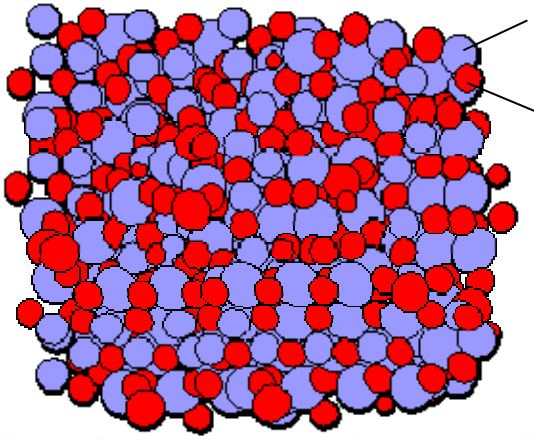


After

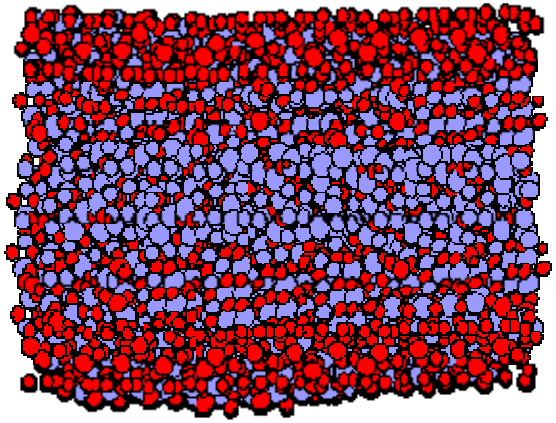
Contact: Darryl Butt, Professor
darrylbutt@boisestate.edu

Phase Distribution Influences Kinetics

Too coarse

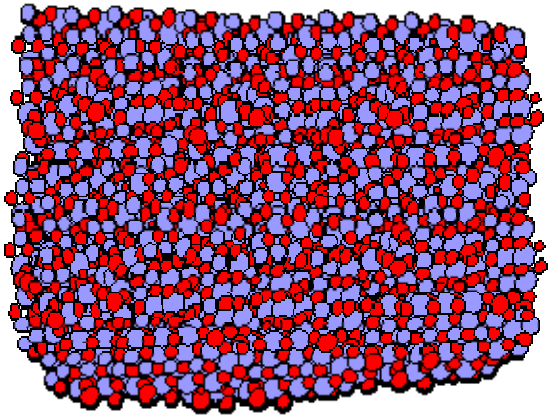


Long heat treatment times may be
Needed to achieve single phase joint



Graded Composition and Fine Particles
Provide Good Wetting and Low Sensitivity
To Heating Rate

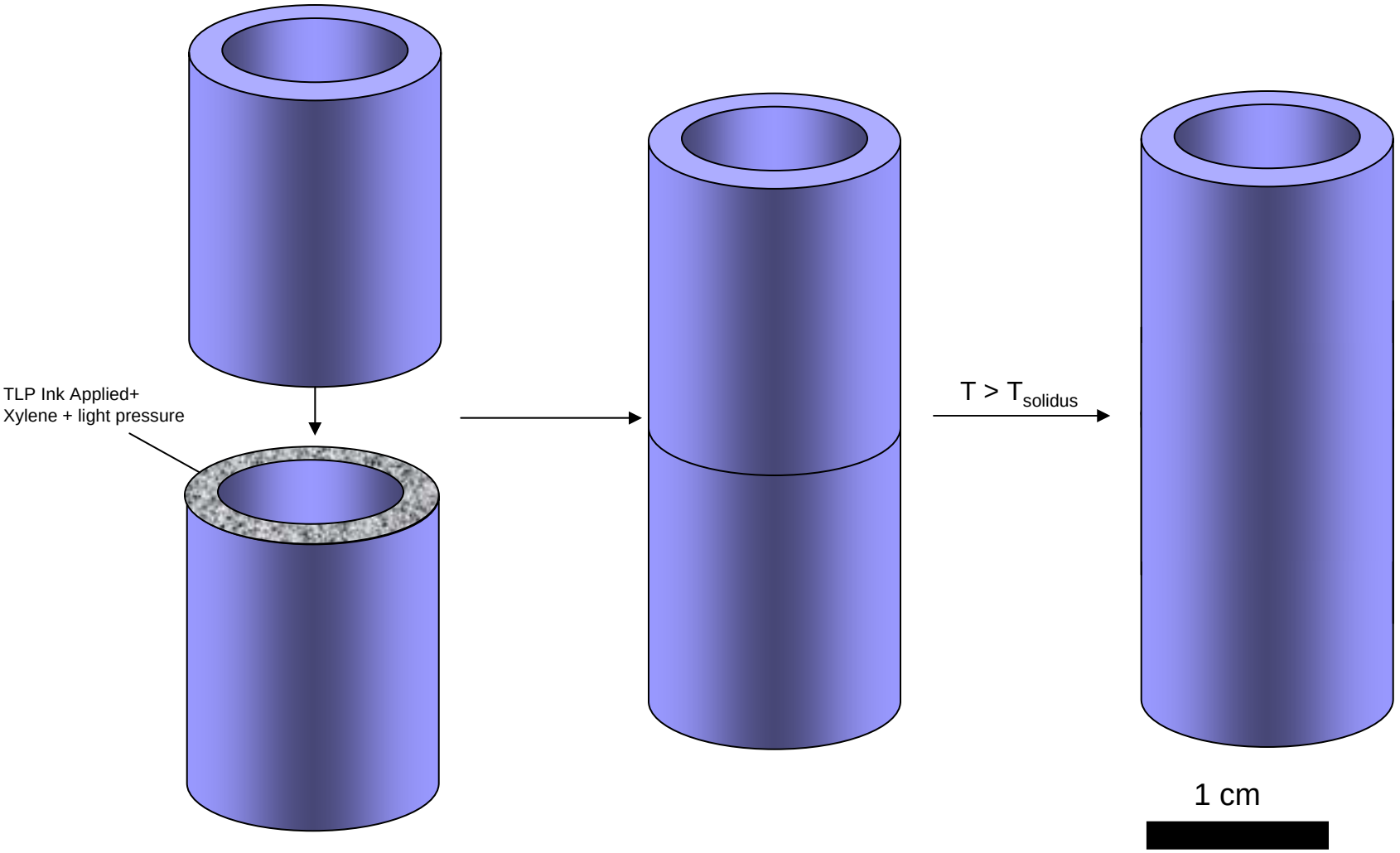
Too fine



Rapid Heating May be Required to Avoid
Premature formation of Refractory Phase

Contact: Darryl Butt, Professor
darrylbutt@boisestate.edu

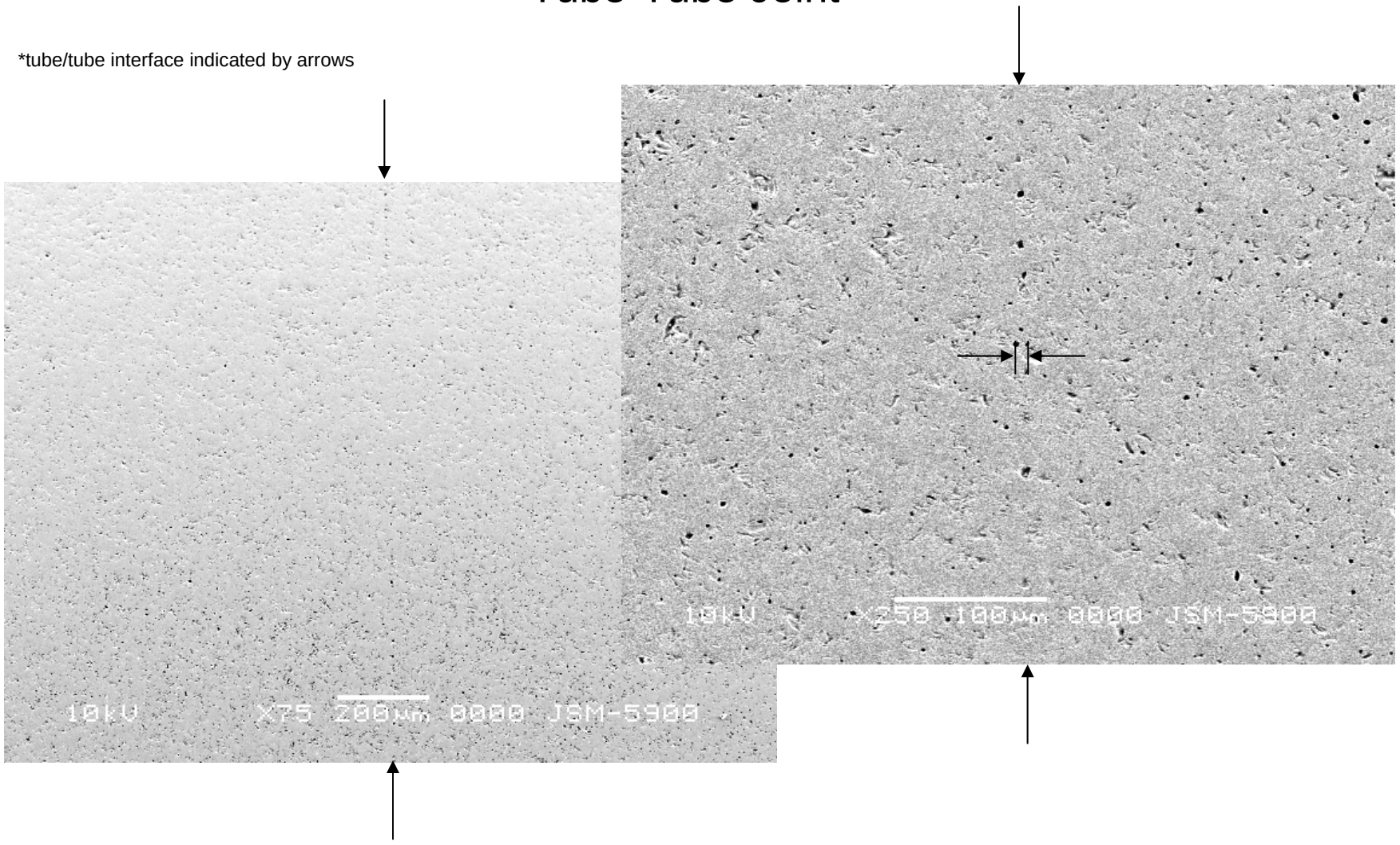
Tube-to-Tube Joining Method



Contact: Darryl Butt, Professor
darrylbutt@boisestate.edu

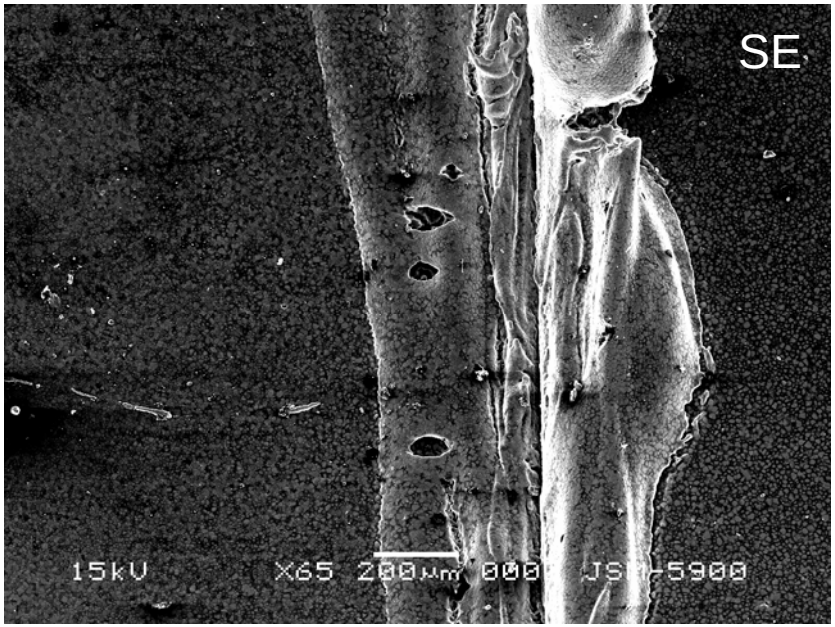
Fully Transient Liquid Phase Tube-Tube Joint*

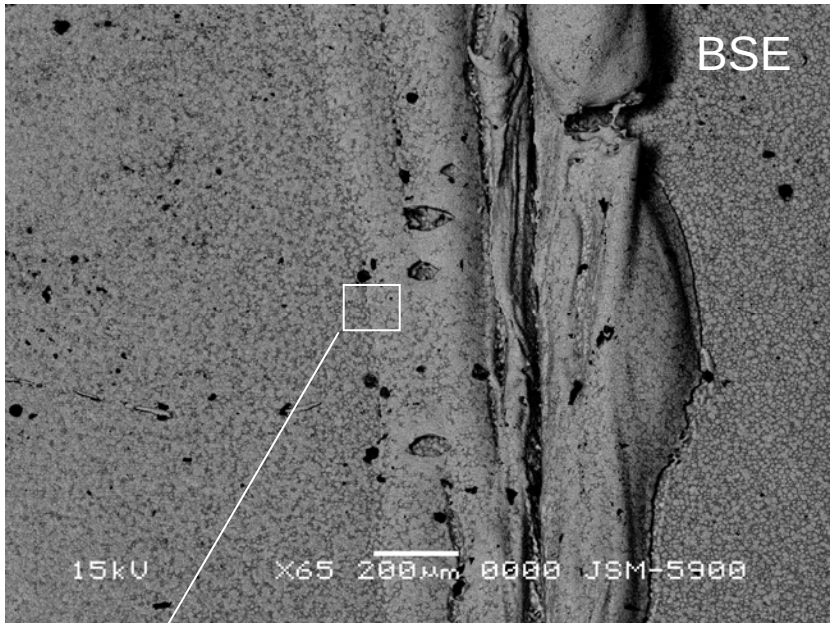
*tube/tube interface indicated by arrows

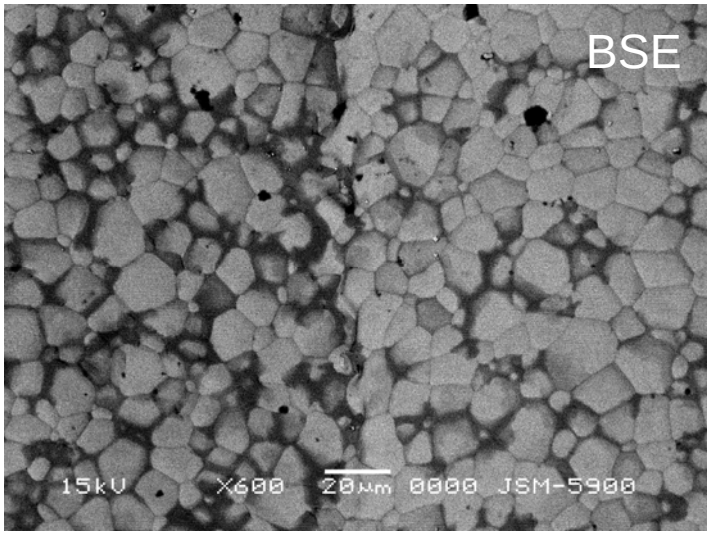


Contact: Darryl Butt, Professor
darrylbutt@boisestate.edu

Overflow of TLP at Tube-Tube Interface



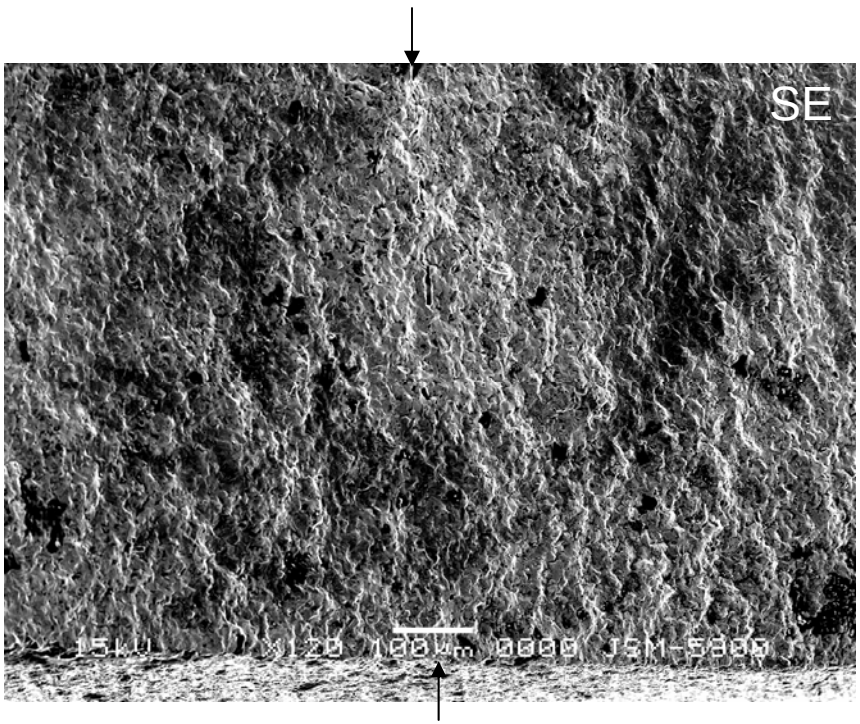


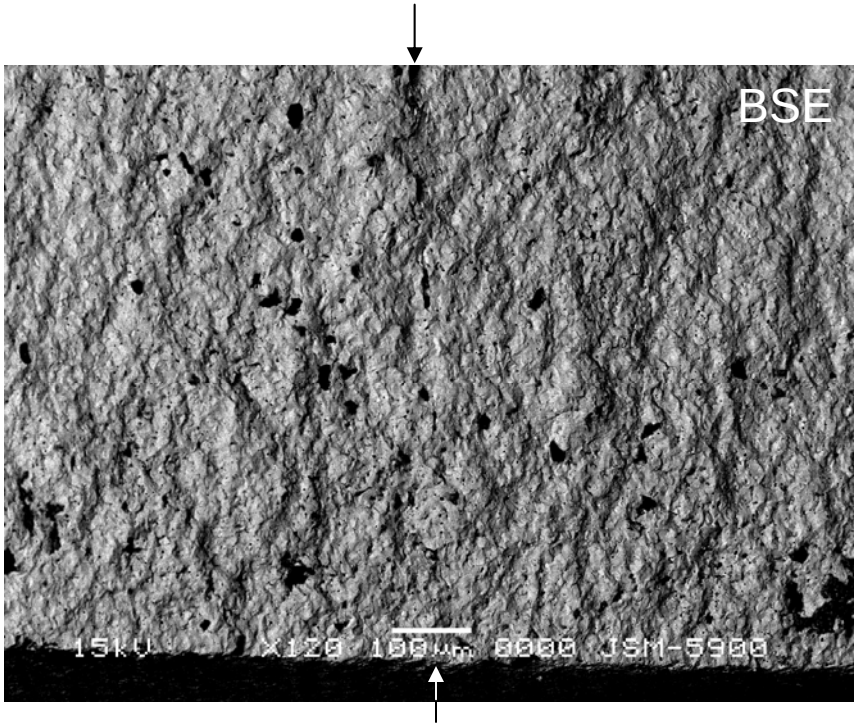


Contact: Darryl Butt, Professor
darrylbutt@boisestate.edu

Fracture Surface Running Through TLP Joint

$La_{.75}Ca_{.25}FeO_{3-x}$

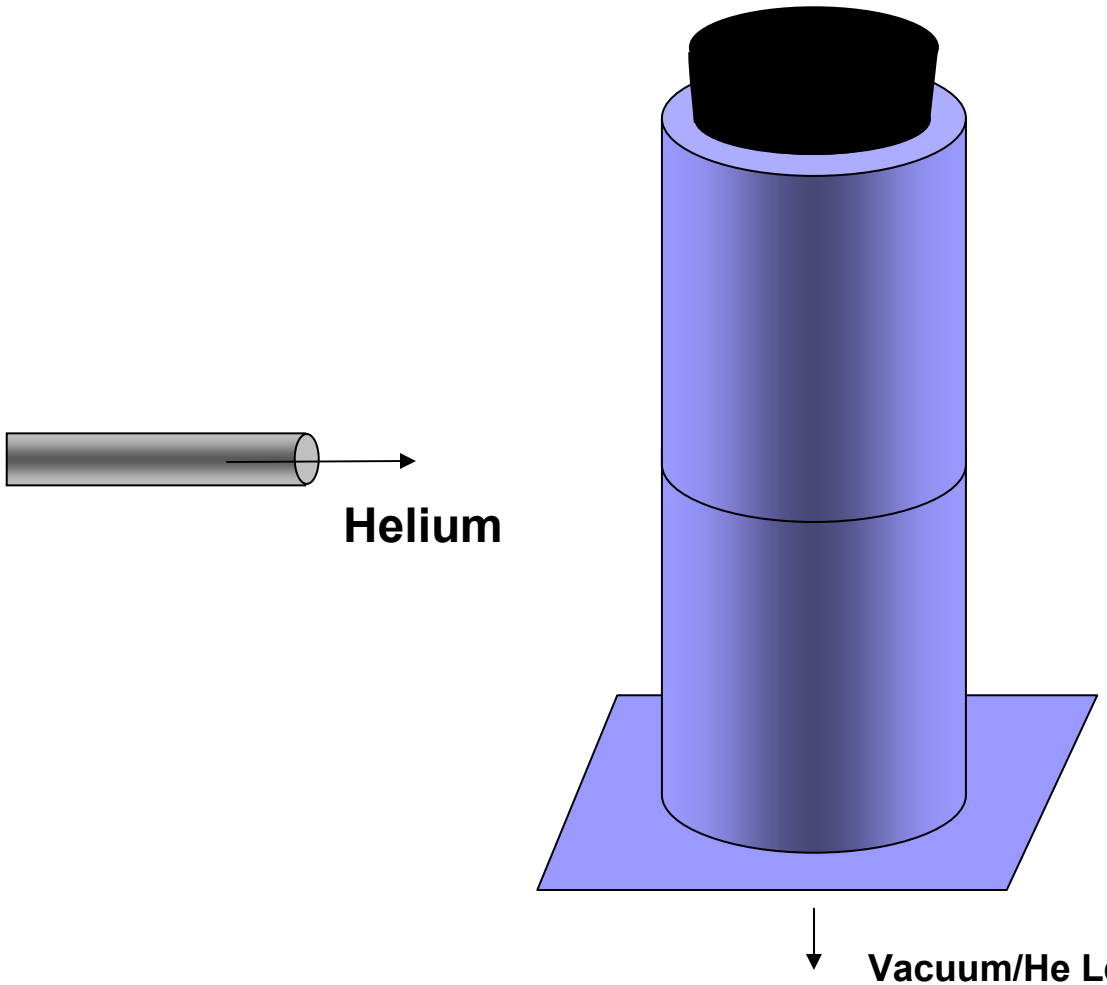




Arrows show location of interface

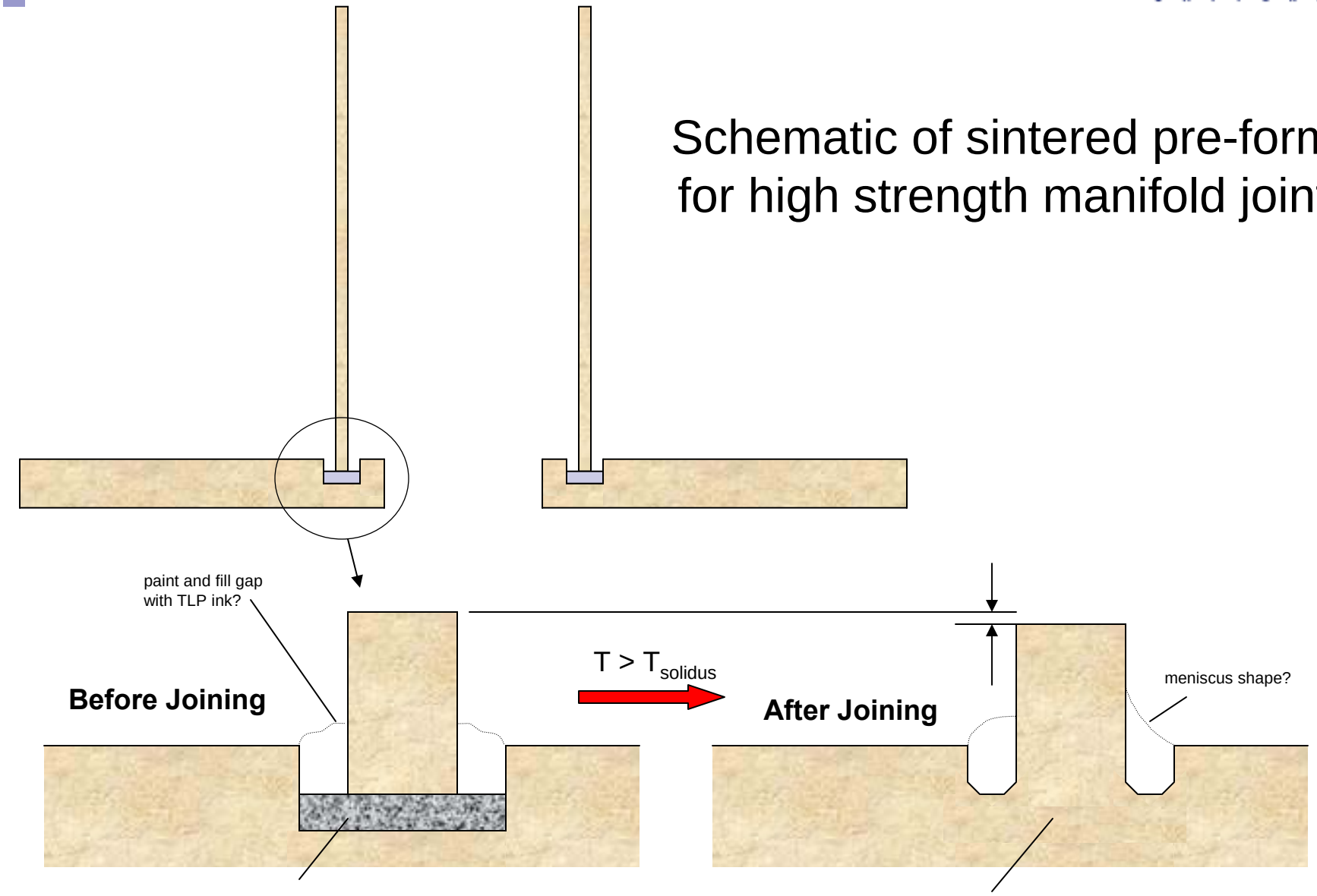
Contact: Darryl Butt, Professor
darrylbutt@boisestate.edu

Helium Leak Testing



Contact: Darryl Butt, Professor
darrylbutt@boisestate.edu

Schematic of sintered pre-form for high strength manifold joint

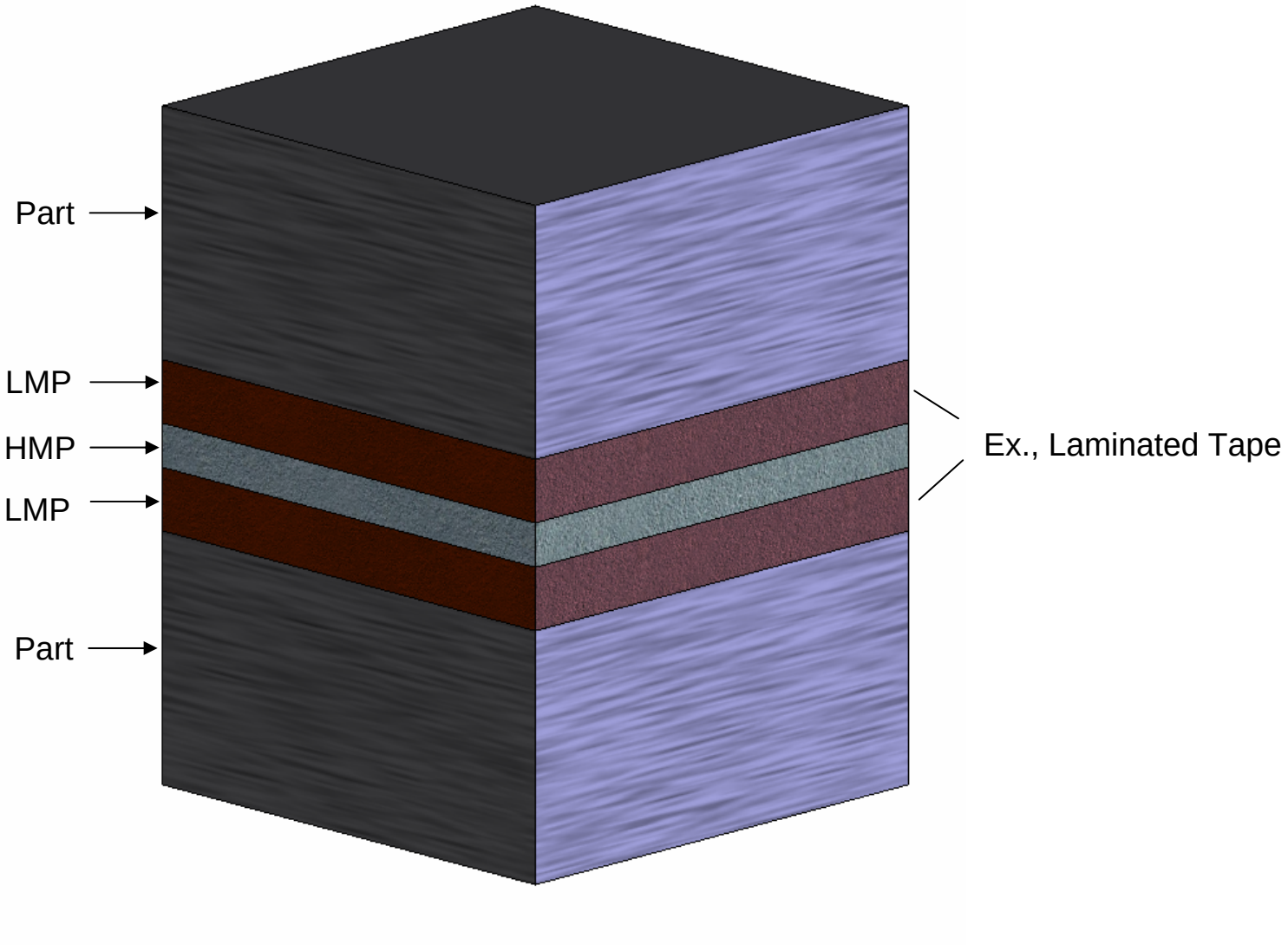


Dense, sintered multiphase TLP preform

Dense, sintered single-phase joint

Contact: Darryl Butt, Professor
darrylbutt@boisestate.edu

Proposed Multilayer Structure



Contact: Darryl Butt, Professor
darrylbutt@boisestate.edu

Concluding Remarks

La-Ca-Fe Based Perovskites Have Been Joined

Attributes Include:

- Fully Transient Liquid Phase
- No Interfacial Phase
- Hermetic to $<10^{-8}$ Torr
- High Strength
- Chemical and Environmentally Compatible
- Very Low Cost
- Very Simple Process
- Ease of Commercialization
- Many Potential Systems

Contact: Darryl Butt, Professor
darrylbutt@boisestate.edu

Continuing Research

- Assess kinetics of refractory phase formation
- Assess A/B Ratio Effects
- Detailed joint characterization
- Tape Development
- Develop Graded Joint
- Demonstrations on Complex Geometries
- Assess Feasibility for Repair
- Develop other Potential Systems
- Commercialization

Contact: Darryl Butt, Professor
darrylbutt@boisestate.edu