"Optimization Of Material For Ceramics And Electronic Applications By Using Molecular Modeling And Design Of Experiment Methods "

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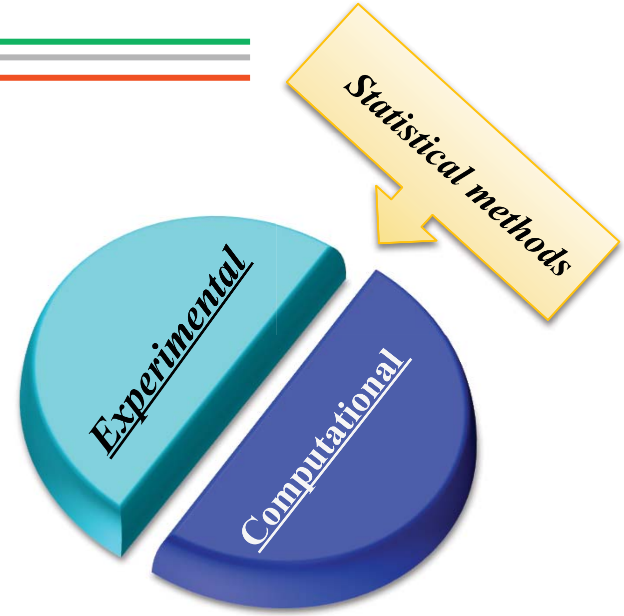
UNIMORE

UNIVERSITÀ DEGLI STUDI DI MODENA E REGGIO EMILIA

REGGIOEMILIA ing

Modeling of Materials (atomistic – mesoscale)

Statistical Methods (DOE, PLS PCA) applied to Materials Design, Process and Technologies



Calatrava's bridge

Application of DOE to tiles production by digital inkjet

Solid State Battery

- **Glass in energy storage**

LEHIGH UNIVERSITY

UNT UNIVERSITY OF NORTH TEXAS

SYSTEM Group

TILE S SAVOIA ITALIA

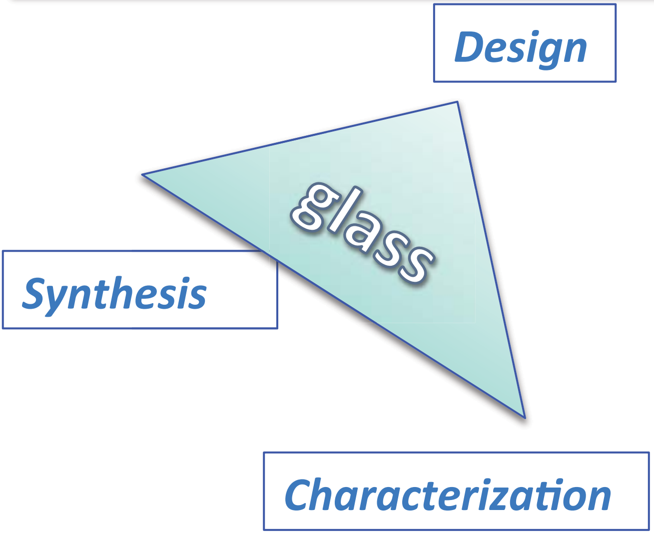
COE COLLEGE

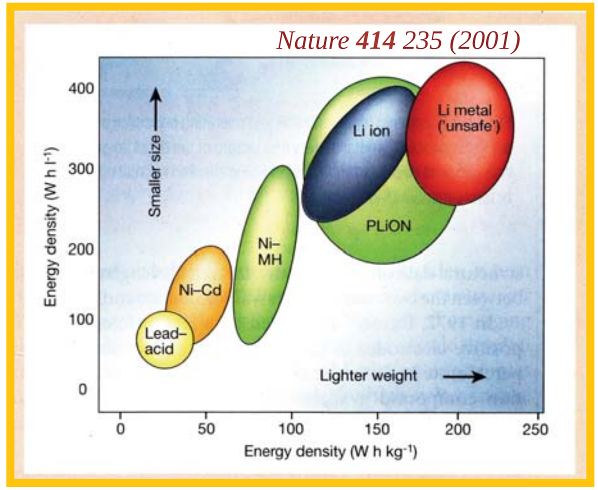
Coe makes it possible. You make it happen.

Solid State Battery

- Glass in energy storage

Solid State Batteries



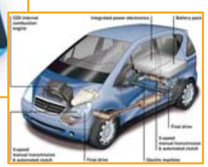


Energy density

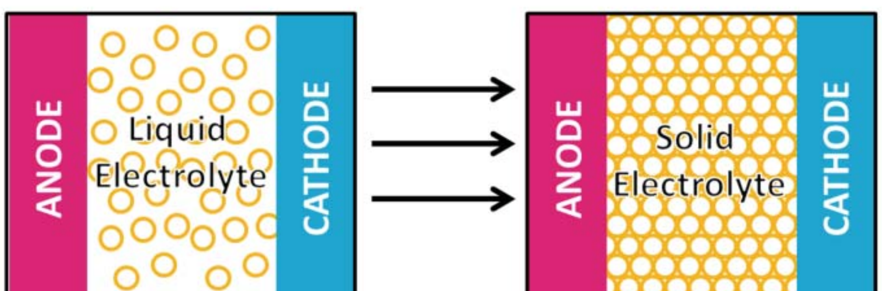
Simple fabrication

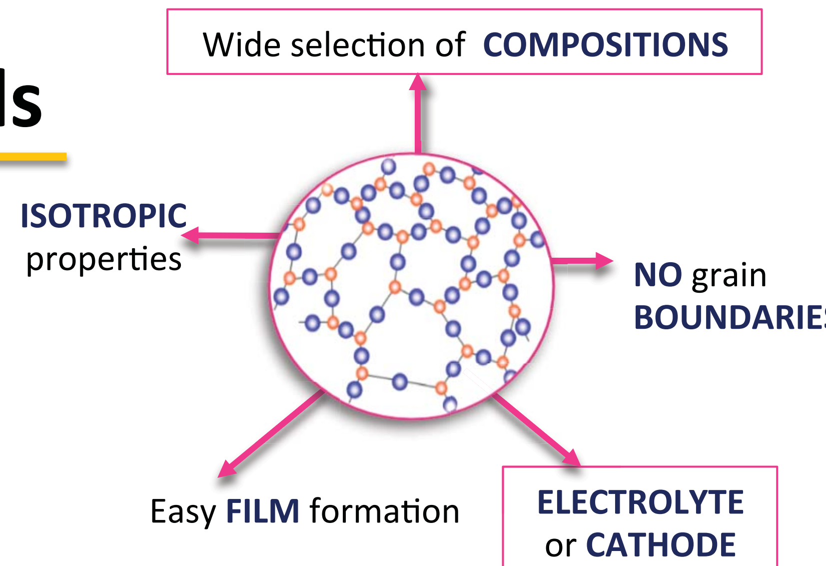
Good safety

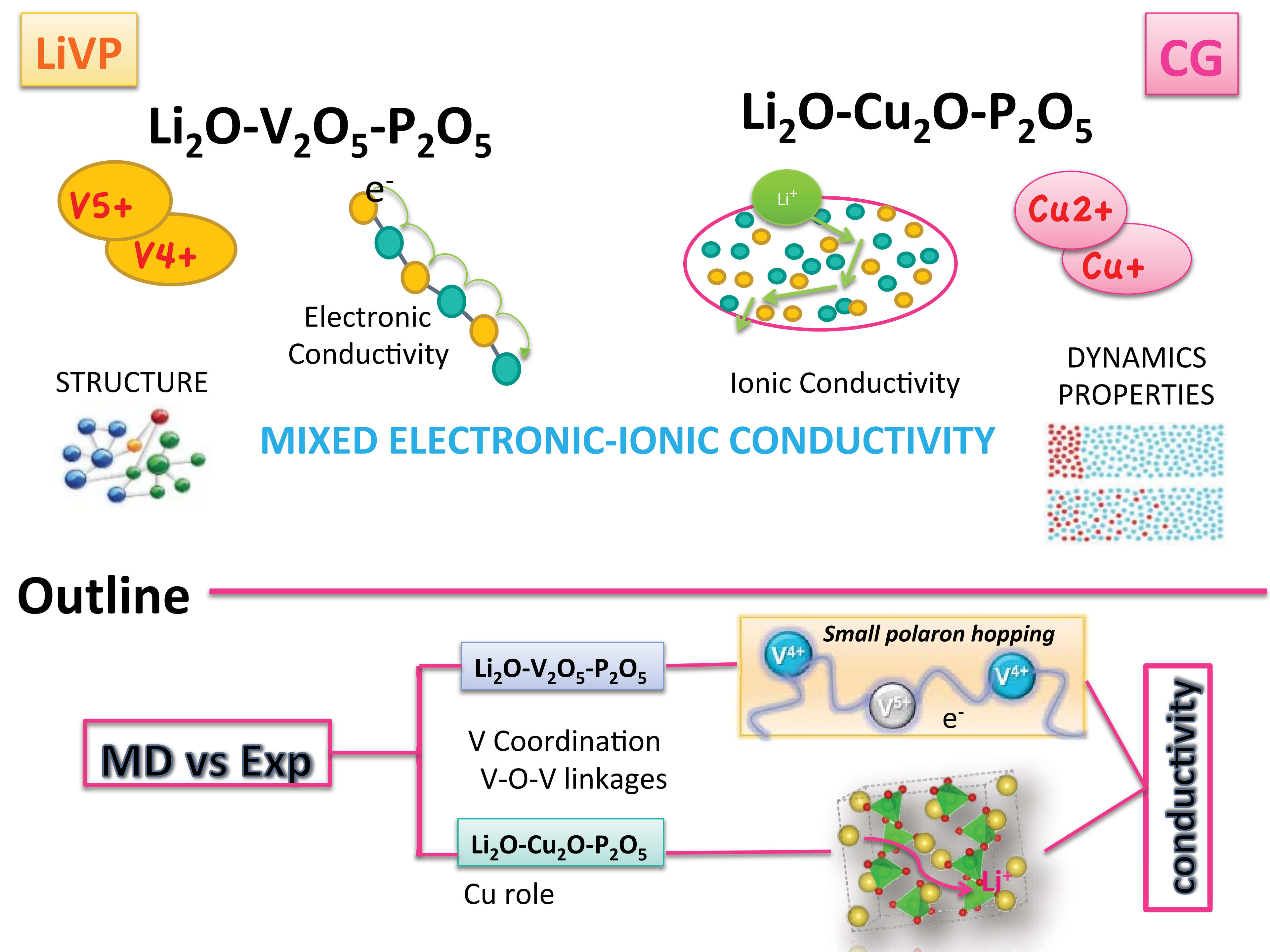
High stability



Glass Materials





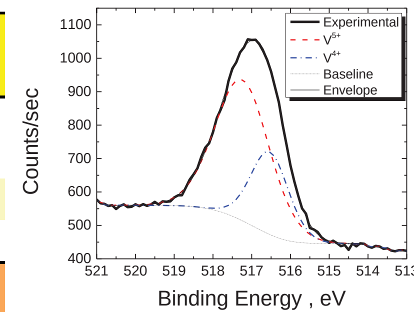


LiVP
CG
Li2O-V2O5-P2O5
Li2O-Cu2O-P2O5
V5+
V4+
e-
Electronic Conductivity
Li+
Cu2+
Cu+
STRUCTURE
Ionic Conductivity
DYNAMICS PROPERTIES
MIXED ELECTRONIC-IONIC CONDUCTIVITY
Outline
MD vs Exp
Li2O-V2O5-P2O5
V Coordination
V-O-V linkages
Li2O-Cu2O-P2O5
Cu role
Small polaron hopping
V4+
V5+
V4+
e-
Li+
conductivity

Methods

LiVP	Li_2O	V_2O_5	P_2O_5	V^{4+}/Vtot	Density (g/cm^3)
LiVP10	45	10	45	0.25	2.58
LiVP30	10	30	60	0.4	2.64
LiVP33	33	33	33	0.26	2.66
LiVP50	10	50	40	0.31	2.78
CG	**Li_2O**	**Cu_2O**	**P_2O_5**	**Cu^{2+}/Cutot**	**Density (g/cm^3)**
CG5	45	5	50	0.72	2.49
CG10	40	10	50	0.84	2.51
CG15	35	15	50	0.8	2.69
CG20	30	20	50	0.82	2.88

G. Broglia, C. Mugoni, J. Du, C. Siligardi, M. Montorsi" *J. Non Cryst. Solids*, , 403, 53-61, **2014**
doi: 10.1016/j.jnoncrysol.2014.07.003

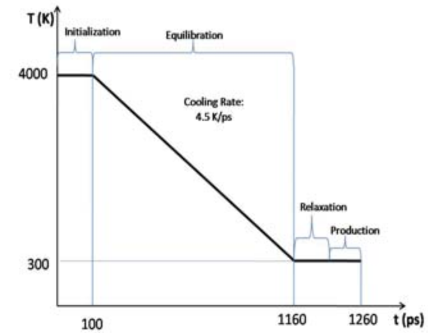


EXP

XPS analysis

MD

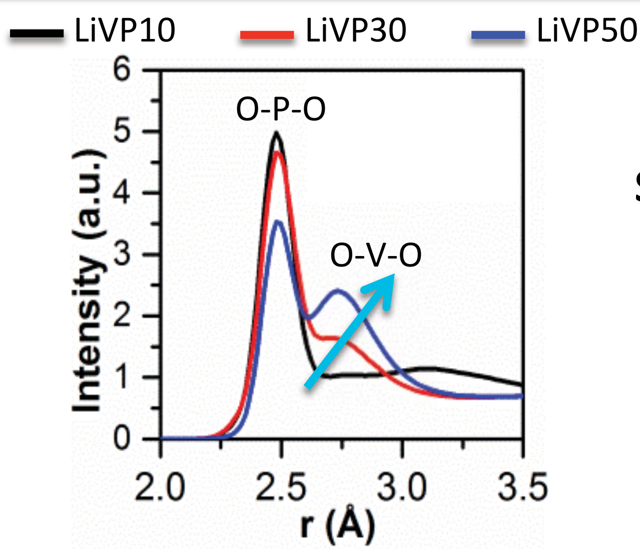
CONVENTIONAL MELT-QUENCH PROCEDURE

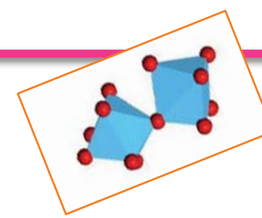


PDF e BAD (short range order)

	V^{4+}-O	V^{5+}-O
LiVP10	1.85	1.92
LiVP30	1.79	1.9
LiVP33	1.74	1.78
LiVP50	1.74	1.81
Ref	1.79[c]	1.79[c]
	1.53-1.97[d]	1.53-1.97[d]

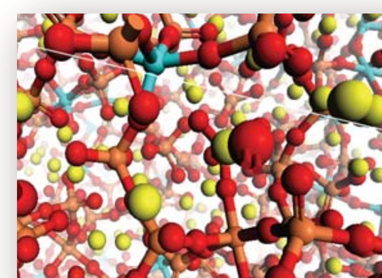
Errors within ±0.005-0.009





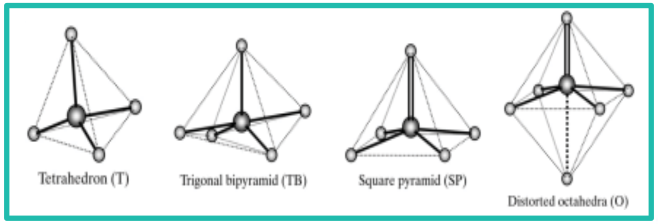
LiVP

Strong distortion of the V based polyhedra



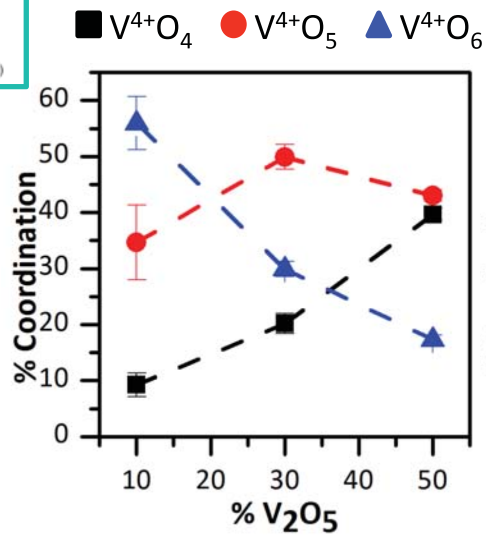
Coordination V

LiVP

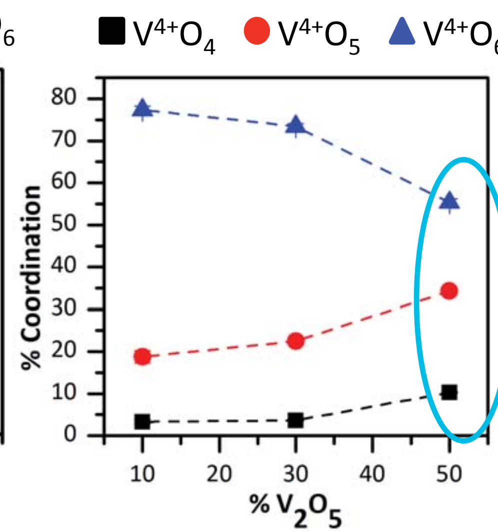


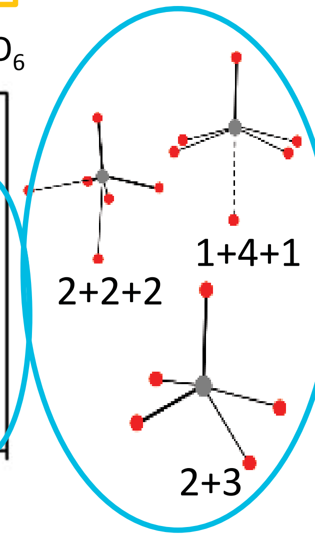
	V^{4+}-O	V^{5+}-O
LiVP10	5.45	5.72
LiVP30	5.10	5.71
LiVP33	5.08	5.68
LiVP50	4.78	5.45

V^{4+}

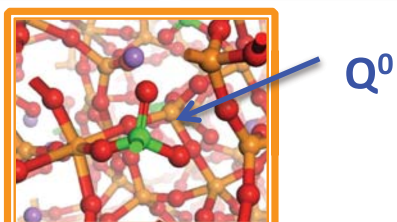


V^{5+}

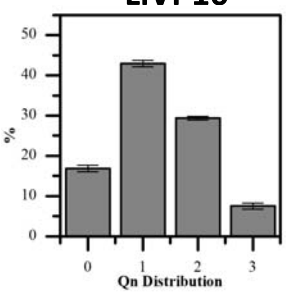




Qn (P) vs Raman (medium range order)

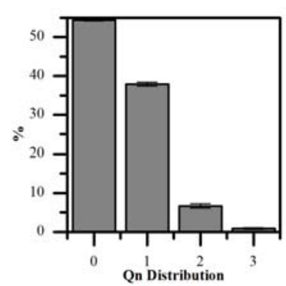


LiVP10



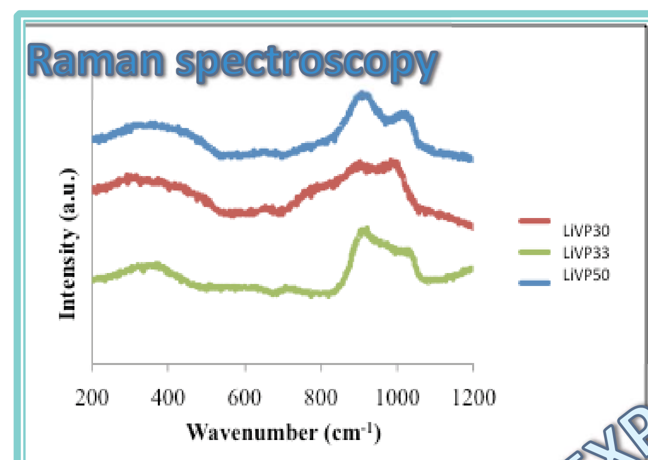
%Cu_2O

LiVP50



P Network

V Network



EXP

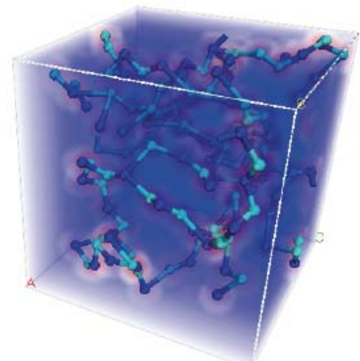
Linkages

LiVP

	V^{4+}/V^{tot}	MD: V^{5+}-O-V^{4+}	P^{5+}-O-P^{5+}	EXP: σ T amb S/cm	σ T=180° S/cm
LiVP10	0.25	0.75	19.81		
LiVP30	0.4	3.9	18.28	$2.79X10^{-9}$	$7.69X10^{-08}$
LiVP33	0.26	6.35	10.2	$3.00X10^{-9}$	$4.30X10^{-06}$
LiVP50	0.31	12.76	4.91	$1.70X10^{-08}$	$1.13X10^{-05}$

✓ Experimental **bulk conductivity increases** when the number of the V^{5+}-O V^{4+} linkages(MD) increase

V^{5+}-O-V^{4+} is independent by the V^{4+}/V^{tot} ratio but is strongly affected by **the structural rearrangement** taking place for increasing content of V_2O_5 in glass composition.



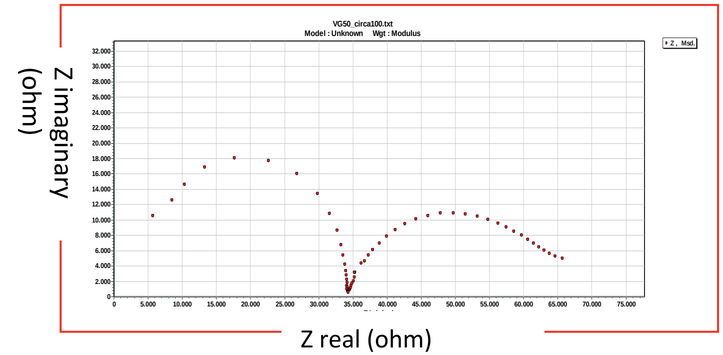
Mixed electronic-ionic conduction

$33Li_2O$-$33V_2O_5$-$33P_2O_5$	*$V^{4+}/Vtot = 0.48$*	*$5X10^{-10}$ S/cm*
glass ceramic β-$LiVOPO_4$		*$1{,}7X10^{-7}$ S/cm*

- *K. Nagamine, T. Honma, T. Komatsu, J. Am. Ceram. Soc., 2008, 91, (12) 3920.*

✓ Conductivity of LiVP33 results one order magnitude more than the correspondent composition in literature.

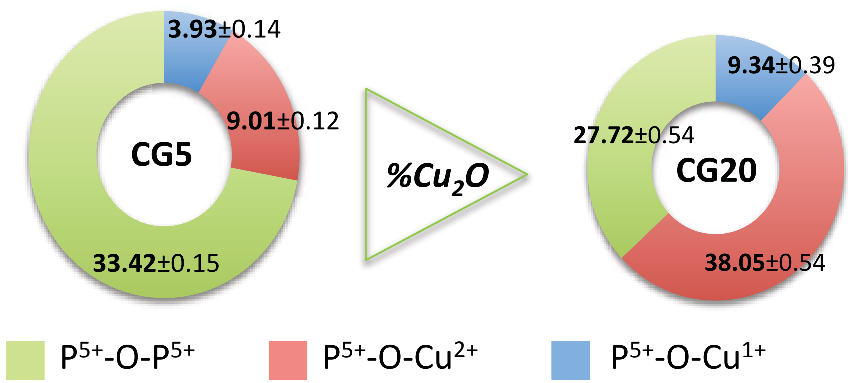
Complex impedance analysis



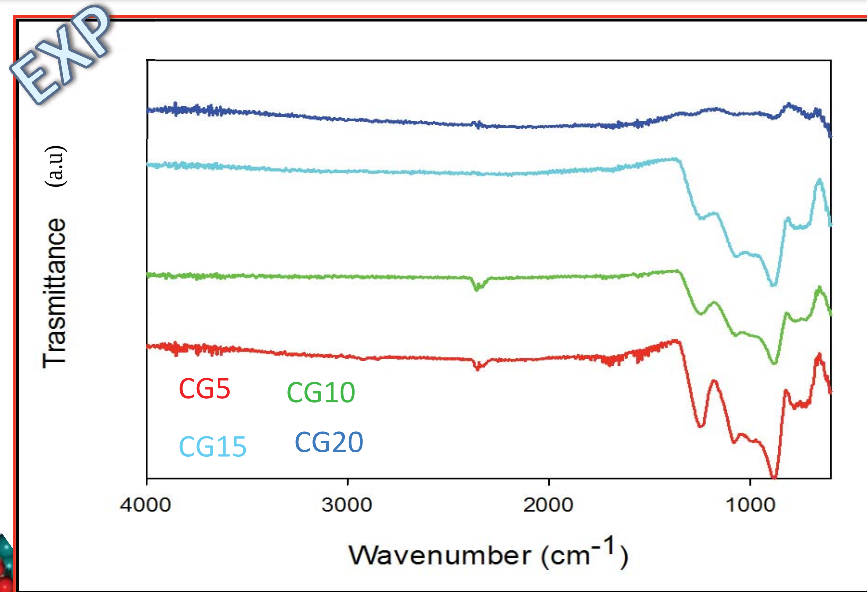
Consuelo Mugoni, Monia Montorsi, Cristina Siligardi, Himanshu Jain Electrical conductivity of copper lithium phosphate glasses, *Journal of Non Crystalline Solids*, 383, 137 -140, **2013**

FTIR vs MD

CG



- **P-O-Cu linkages at the expenses of the P-O-P**
- The main contribution in **P-O-Cu derives from the P-O-Cu^{2+}**

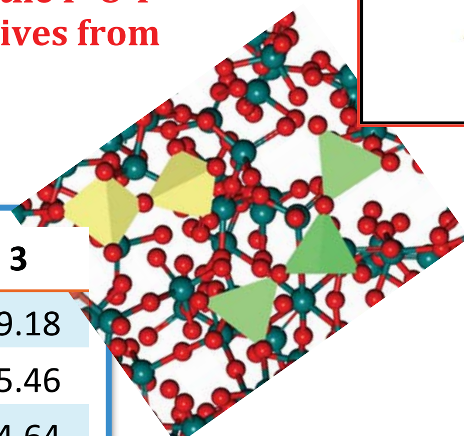


1088 cm^{-1} — **Intensity decreases** can be attributed to the existence of **P - O - Cu bonds**

1265 cm^{-1} — **The decrease of $(PO_2)_{as}$** intensity confirms that the ($^-$O-)P-O^- ··· Li^+ bonds are substituted by **P-O-Cu** bonds when Li_2O is replaced by Cu_2O.

890 cm^{-1} — The **intensity decreases** could be associated to a **depolymerization** of phosphate chains.

MD



Qn	0	1	2	3
CG5	2.42	25.05	48.13	19.18
CG10	3.66	28.09	48.46	15.46
CG15	4.13	32.14	44.48	14.64
CG20	4.50	35.62	44.70	12.27

✓ Slight **depolymerization** dependent of the Cu_2O content.

NBO/NBO+BO	*CG5*	*CG10*	*CG15*	*CG20*
EXP	0.63	0.63	0.71	0.71
MD	0.66	0.69	0.71	0.72

error ± 3%

A. Mogus-Milankovic et al. "Structural and electrical properties of Li_2O-ZnO-P_2O_5 glasses" Journal of Non-Crystalline Solids 536, (2010), 715-719

P.Y. Shih, J.Y. Ding, S.Y. Lee Materials Chemistry and Physics 80 (2003) 391-396 "

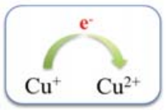
CONDUCTIVITY MEASUREMENTS

CG

Two possible conduction mechanism

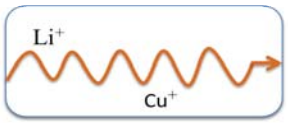
Electron hopping

From Cu^{+} to Cu^{2+}

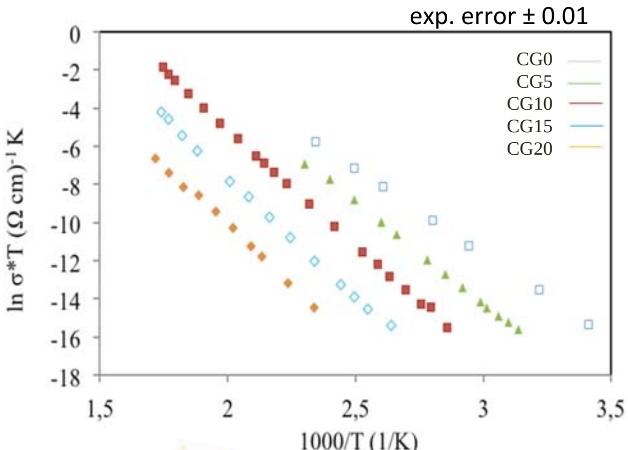


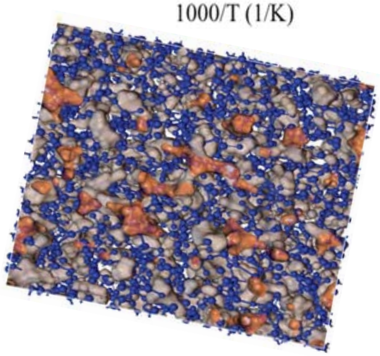
Ionic conductivity

Li^{+} and Cu^{+} migration



Arrhenius equation $\sigma T = \sigma_0 \exp(E_{dc}/kT)$

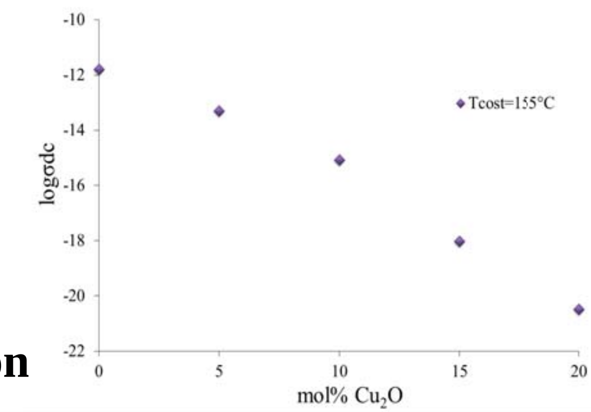


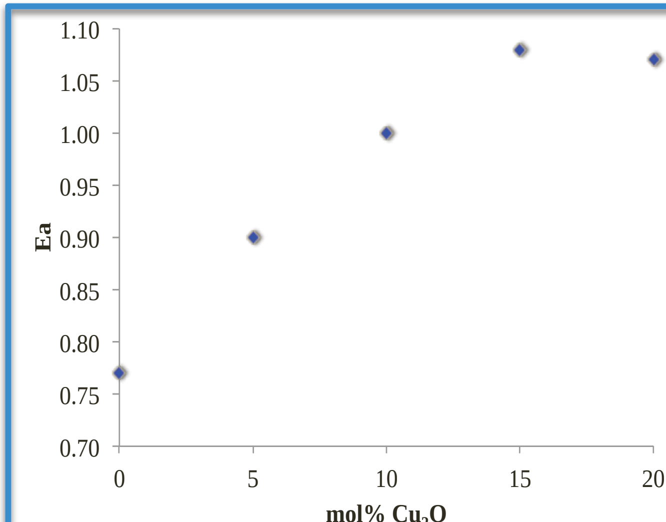


The conductive value **decreases (2 order of magnitude)** with the increase in copper oxide content

ionic conduction

Conductivity vs Cu_2O mol%





concentration-dependent activation energy

Copper Effect

classic mixed mobile ions effect **(MMIE)**

- *(Ionic conductivity - In agreement with Li-Zn-P2O5 glasses*
- "Crystallization Process and Mixed Alkali Effect in Lithium-Potassium Borate Glass"

DIFFUSION ANALYSIS

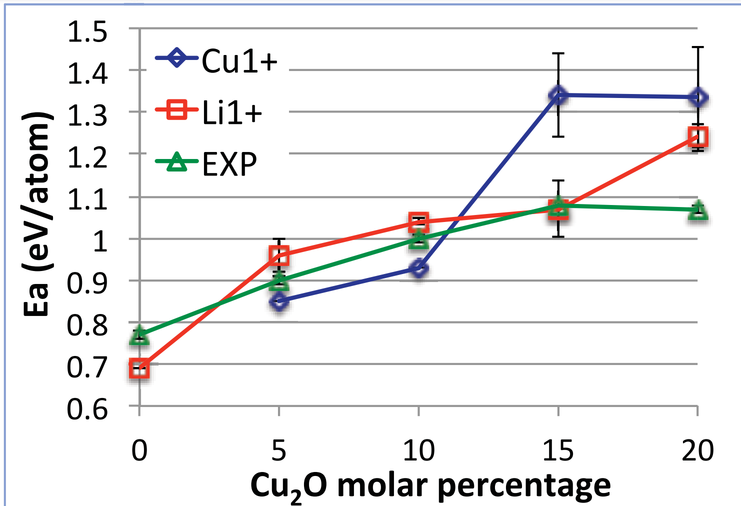
CG

Mobile ion

Only Cu^+

Only Li^+

$Li^+ + Cu^+$



MD

Ionic conductivity due to the Li^+ diffusion in glass structure

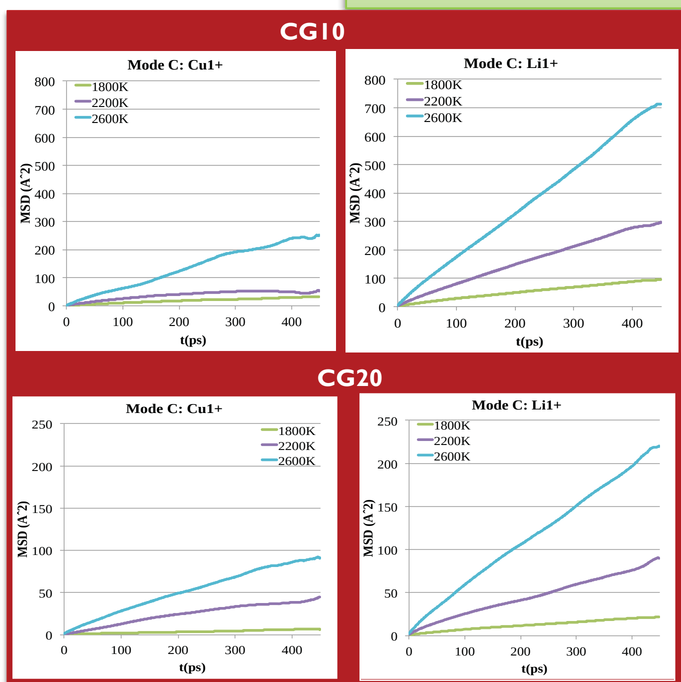
	CG5	CG10	CG15	CG20
Cu^{1+}-O-Cu^{2+}	0.22±0.03	0.49±0.09	1.66±0.07	2.00±0.58

The diffusion of Li^+ promotes the diffusion of Cu^+ in the glass network

The diffusion of **Li^+ ions is higher than Cu^+** in all glasses

The increase of **Cu_2O content leads to a decrease of both Cu^+ and Li^+ motion.**

MMIE



The amount of Cu^{1+}-O-Cu^{2+} <u>remains too small</u> to create conductive path in the systems,

NO ELECTRONIC CONTRIBUTION

Conclusion

- From P_2O_5 network to V_2O_5 network

Increase of V_2O_5 content

Increase of V_2O_5 / P_2O_5 ratio

LiVP

- Linear increase of V-O-V linkages

Increased electronic contribution

Work in progress

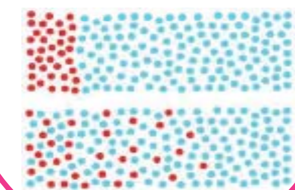
Cu_2O-V_2O_5-Te_2O_3

10^{-5} S/cm
T room

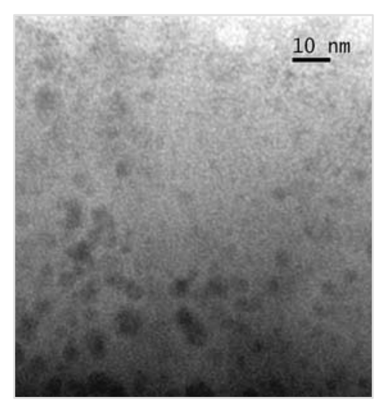
presence of P-O····Cu bonds

Ionic conductivity: Lithium diffusion with a MMIE

CG



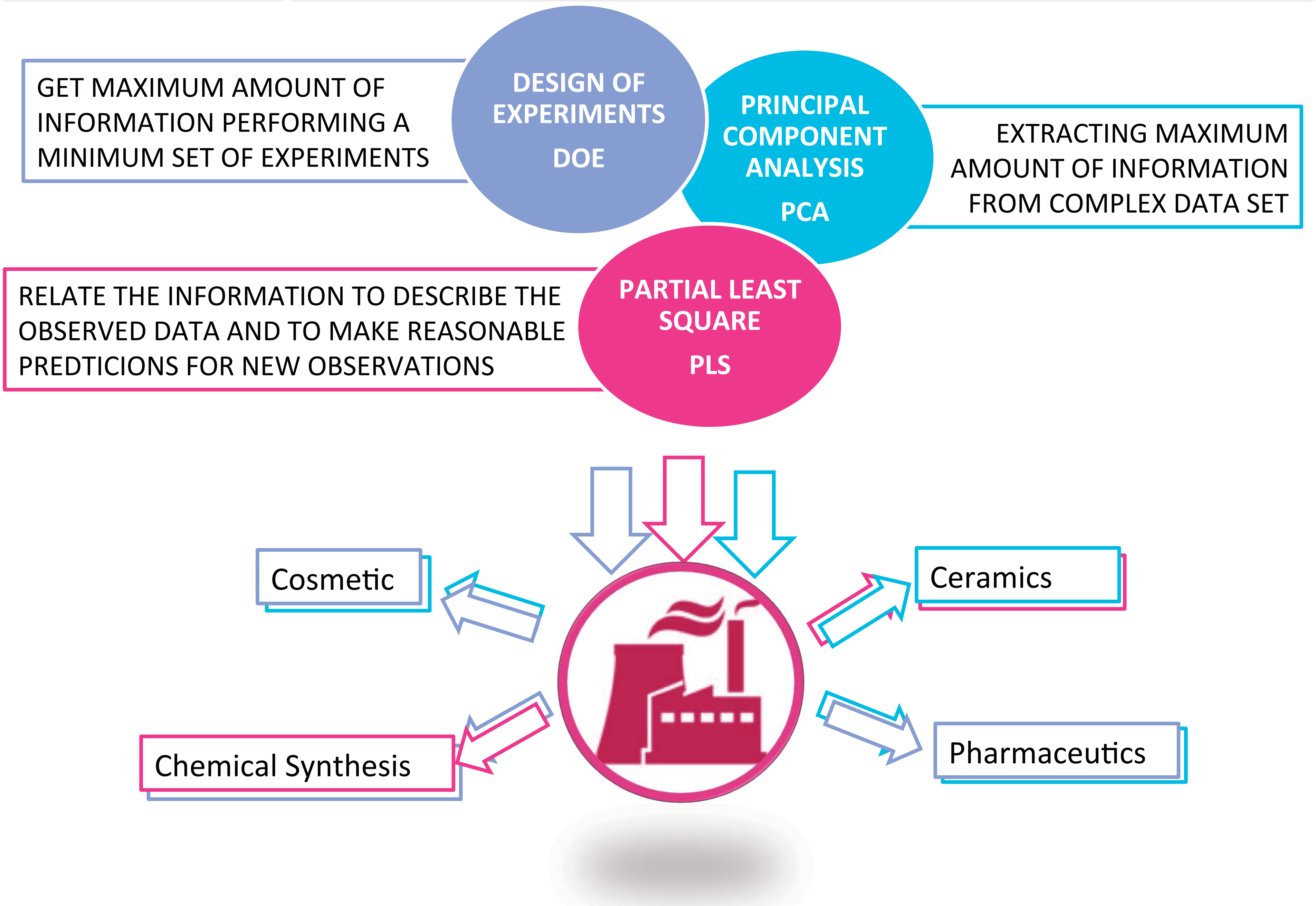
Work in progress



Cu^0 nanoparticles in glass matrix

Application of DOE to design and production of ceramic tiles

Multivariate Statistical Methods



Design of Experiment

Design of Experiment

1. Aims

Reduction of time and cost process
Improve the performance and the product quality
Improve process control

2. Response Variables

Quantity and quality properties of final product, time and cost of the process

3. Factors

Raw materials
Process Parameters
Uncontrallable variables

4. Models

Screening
Optimization
Model Validation

5. Collecting Data

Worksheet
Random experiments
Best practies

6. Analysis

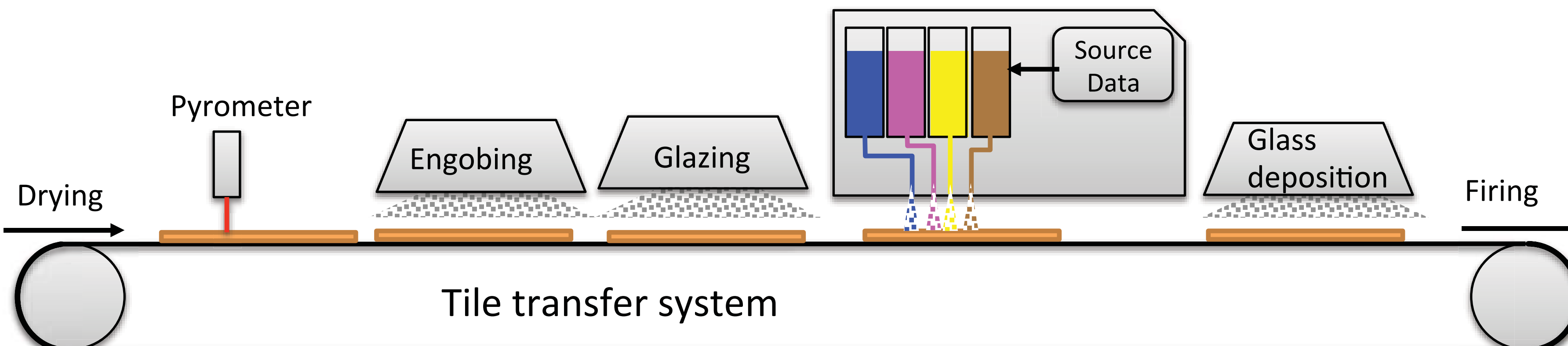
ANOVA
Response Surface
Fitting Model

Case Study

Improve Quality

Improve Control

Tile Manufacturing & Digital Ink-jet printing



PROCESS MAP

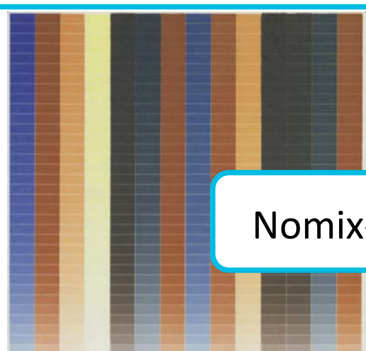
7 VARIABLES		RANGE
T of green body	[TGB]	80-110 °C
Engobe thickness	[TH1]	40-60 gr
Glaze thickness	[TH2]	10-30 gr
Glaze Type	[GTY]	SM963-SM918B
Printer resolution	[DPI]	200-400 dpi
Glass thickness	[TH3]	10-30
Max T of Firing Cycle	[TMX]	1200-1210 °C

INPUT

IN-LINE TILE PRODUCTION

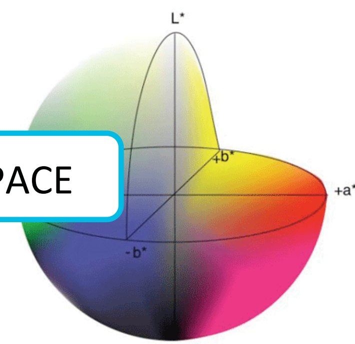
BEST PRACTIES

RESPONSES



Nomix- Target tile

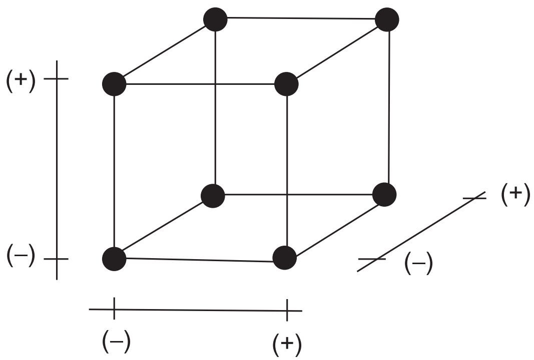
CIELab SPACE



PANEL TEST

DOE APPROACH

Experimental Domain



FULL

factorial 2^K

FRACTIONAL

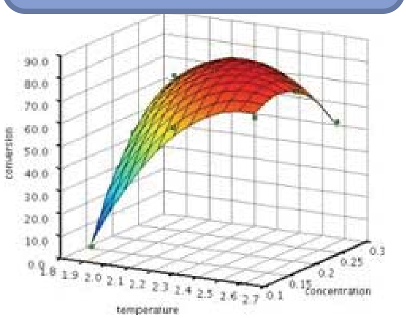
factorial 2^{K-P}

128 TESTs

SCREENING DESIGN

30 TESTs

Model



Linear Model

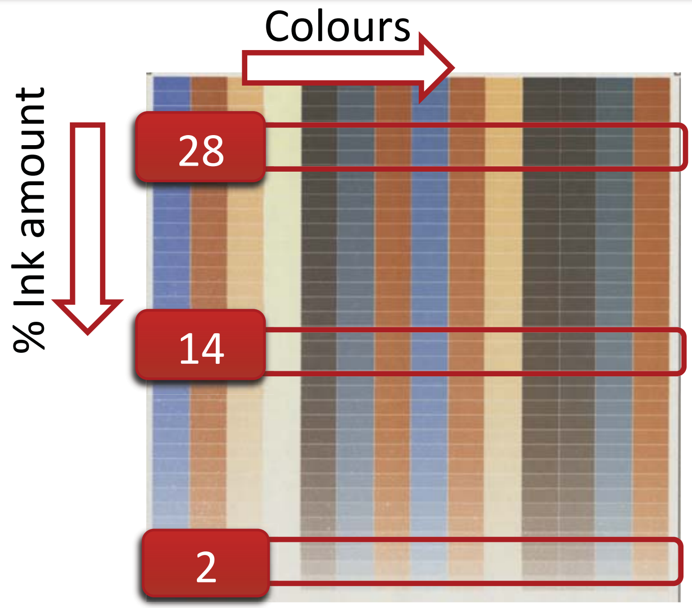
$$y = \boldsymbol{\beta_0} + x_1\,\boldsymbol{\beta_1} + x_2\,\boldsymbol{\beta_2} + \ldots + x_n\,\boldsymbol{\beta_n} + x_{1,2}\,\boldsymbol{\beta_{1,2}} + x_{1,3}\,\boldsymbol{\beta_{1,3}} + \ldots + \varepsilon$$

Response Variables

CIELab SPACE

GOAL: HOW TO CONTROL THE COULOR QUALITY

L*	black	⟷	white
a*	green	⟷	magenta
b*	blue	⟷	yellow



1.Cyan
2.Brow
3. Beige
4. Yellow
5. 1+2
6. 1+3
7. 2+3
8. 1+4
9. 2+4
10. 3+4

PANEL TEST

GOAL: HOW TO PREVENT DEFECT FORMATION

WHITE DOTS

STAINS

ROUGHNESS

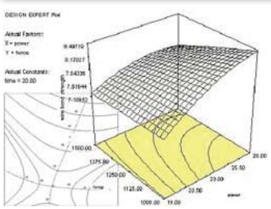
CIELab: MOST INFLUENTIAL VARIABLES

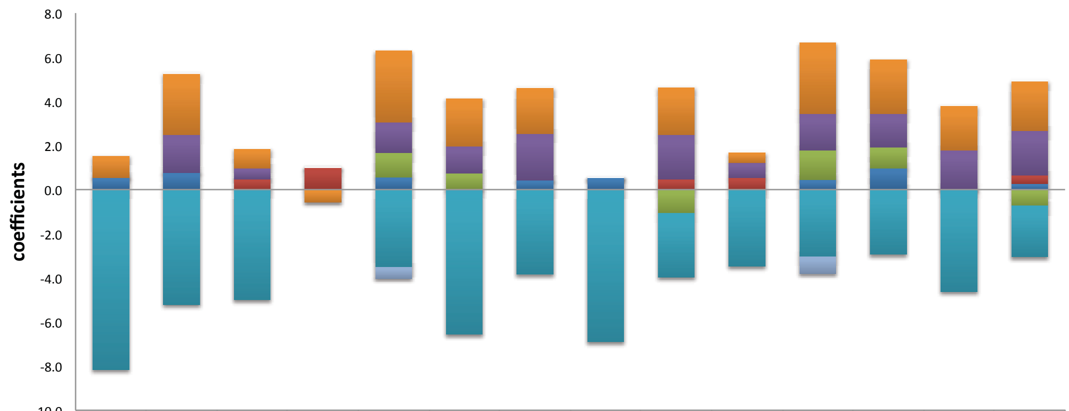
	TGB	TH1	TH2	GTY	DPI	TH3	TMX
L		✔	✔		✔	✔	
a			✔	✔	✔	✔	
b		✔	✔	✔	✔	✔	

7 VARIABLES

T of green body [TGB]
Engobe thickness [TH1]
Glaze thickness [TH2]
Glaze type [GTY]
Printer resolution [DPI]
Glass thickness [TH3]
Max T of Firing Cycle [TMX]

MODELS





	L28-1	L28-2	L28-3	L28-4	L28-5	L28-6	L28-7	L28-8	L28-9	L28-10	L28-11	L28-12	L28-13	L28-14
TMX	0.0	0.0	0.0	0.0	-0.5	0.0	0.0	0.0	0.0	0.0	-0.8	0.0	0.0	0.0
TH3	1.0	2.7	0.9	-0.6	3.2	2.2	2.0	0.0	2.1	0.4	3.2	2.4	2.0	2.2
DPI	-8.2	-5.2	-5.0	0.0	-3.5	-6.6	-3.8	-6.9	-2.9	-3.5	-3.1	-2.9	-4.6	-2.3
GTY	0.0	1.7	0.5	0.0	1.4	1.2	2.1	0.0	2.0	0.7	1.7	1.5	1.8	2.0
TH3	0.0	0.0	0.0	0.0	1.1	0.7	0.0	0.0	-1.1	0.0	1.3	0.9	0.0	-0.7
TH1	0.0	0.0	0.5	1.0	0.0	0.0	0.0	0.0	0.5	0.5	0.0	0.0	0.0	0.4
TGB	0.5	0.8	0.0	0.0	0.5	0.0	0.4	0.5	0.0	0.0	0.4	1.0	0.0	0.3

Weights of the variables coefficients : for L28 the printer resolution (dpi) increasing lead to the luminosity decrease.

$y = \boldsymbol{\beta_0} + x_1\,\boldsymbol{\beta_1} + x_2\,\boldsymbol{\beta_2} + \dots + x_n\,\boldsymbol{\beta_n} + x_{1,2}\,\boldsymbol{\beta_{1,2}} + x_{1,3}\,\boldsymbol{\beta_{1,3}} + \dots + \varepsilon$

CIELab: MOST INFLUENTIAL VARIABLES

L28

Influential Variables	Most affected colours	Less Affected colours
DPI (-) GTY (+) TH3 (+)	1 cyan 2 brown 5 brown+ciano 6 cyan+beige 11 ciano+brown+beige	4 yellow 10 beige+giallo

L14

Influential Variables	Most affected colours	Less Affected colours
DPI (-) GTY (+) TH3 (+)	1 cyan 2 brown 5 brown+cyan 7 brown+beige 11 cyan+braown+beige	4 yellow 3 beige 10 beige+yellow

L2

Influential Variables	Most affected colours	Less Affected colours
DPI (-) → TH2 (-) TH3 (+) → TH1 (+)	5 brown+cyan 6 cyan+beige 11 cyan+brown+beige 12 brown+yellow+cyan	4 yellow 3 beige 10 beige+yellow

7 VARIABLES

T of green body	[TGB]
Engobe thickness	[TH1]
Glaze thickness	[TH2]
Glaze type	[GTY]
Printer resolution	[DPI]
Glass thickness	[TH3]
Max T of Firing Cycle	[TMX]

DEFECT: MOST INFLUENTIAL VARIABLES

	TGB	TH1	TH2	GTY	DPI	TH3	TMX
White Dots	✔		✔		✔	✔	
Stains				✔	✔	✔	
Rougness			✔	✔	✔	✔	

7 VARIABLES	
T of green body	[TGB]
Engobe thickness	[TH1]
Glaze thickness	[TH2]
Glaze type	[GTY]
Printer resolution	[DPI]
Glass thickness	[TH3]
Max T of Firing Cycle	[TMX]

BEST OPERATING CONDITION

WHITE DOTS

T of green body.............. 80
Glaze thickness.............. 30
Printer resolution.......... 400
Glass thickness.............. 10

STAINS

Glaze type.................. SM693
Printer resolution....... 200
Glass thickness........... 10

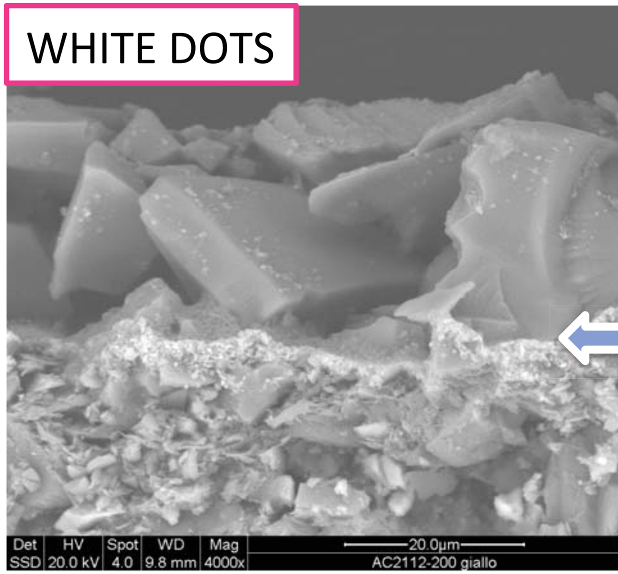
ROUGHNESS

Glaze thickness.......... 30
Glaze type.................. SM693
Printer resolution....... 200
Glass thickness............ 10

CAUSE-EFFECT RELATIONS

	TGB	TH1	TH2	GTY	DPI	TH3	TMX
White Dots	✔		✔		✔	✔	
Stains				✔	✔	✔	
Rougness			✔	✔	✔	✔	

WHITE DOTS

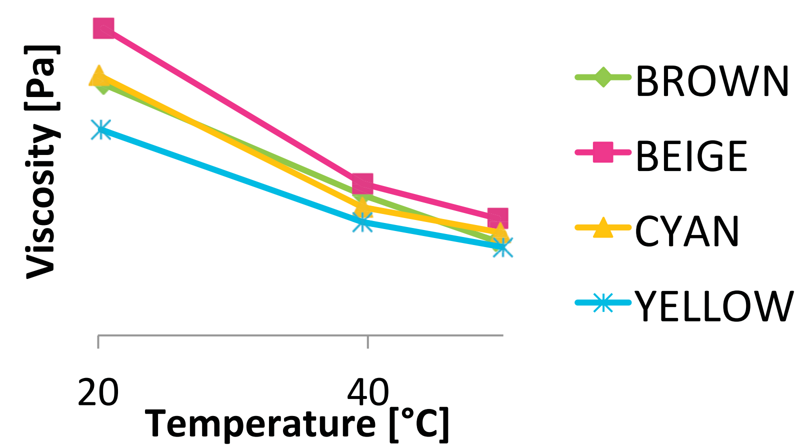


Glassy:
Glass fraction

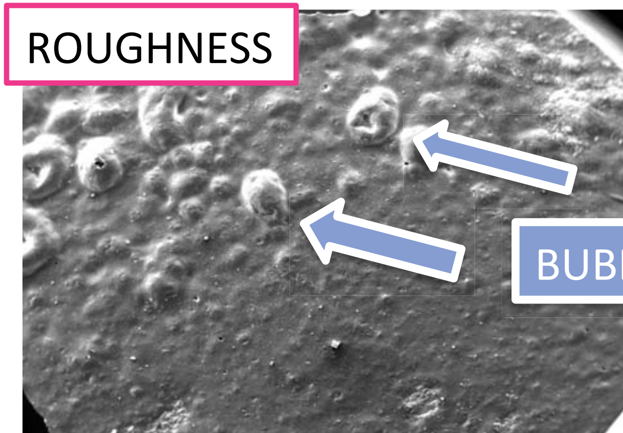
Ink

Glassy:
Clay fraction

Ink viscosity Vs Temperature



ROUGHNESS



BUBBLE

BUBBLES FORMATION DUE TO THE NOT SUITABLE VISCOSITY OF SM918 GLAZE

STAINS FORMATION DUE TO THE NOT SUITABLE SURFACE TENSION OF SM918 GLAZE

STAINS