Low Temperature Formation of NZP Ceramics

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Objective

To investigate chemical routes toward making NZP ceramics at low temperature ($<1000^{o}$C).

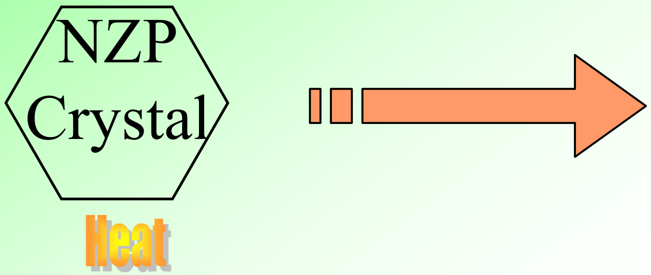
To be able to tune or control such properties as:

- Shrinkage upon firing
- Porosity/Surface Area
- Microstructure
- Mechanical Strength

Why NZP?

- Near-Zero Thermal Expansion (tunable)
- High Thermal Shock Resistance
- High Temperature Stability
- High Insulating Qualities
- Can be Formed at Low Temperatures

Thermal Expansion

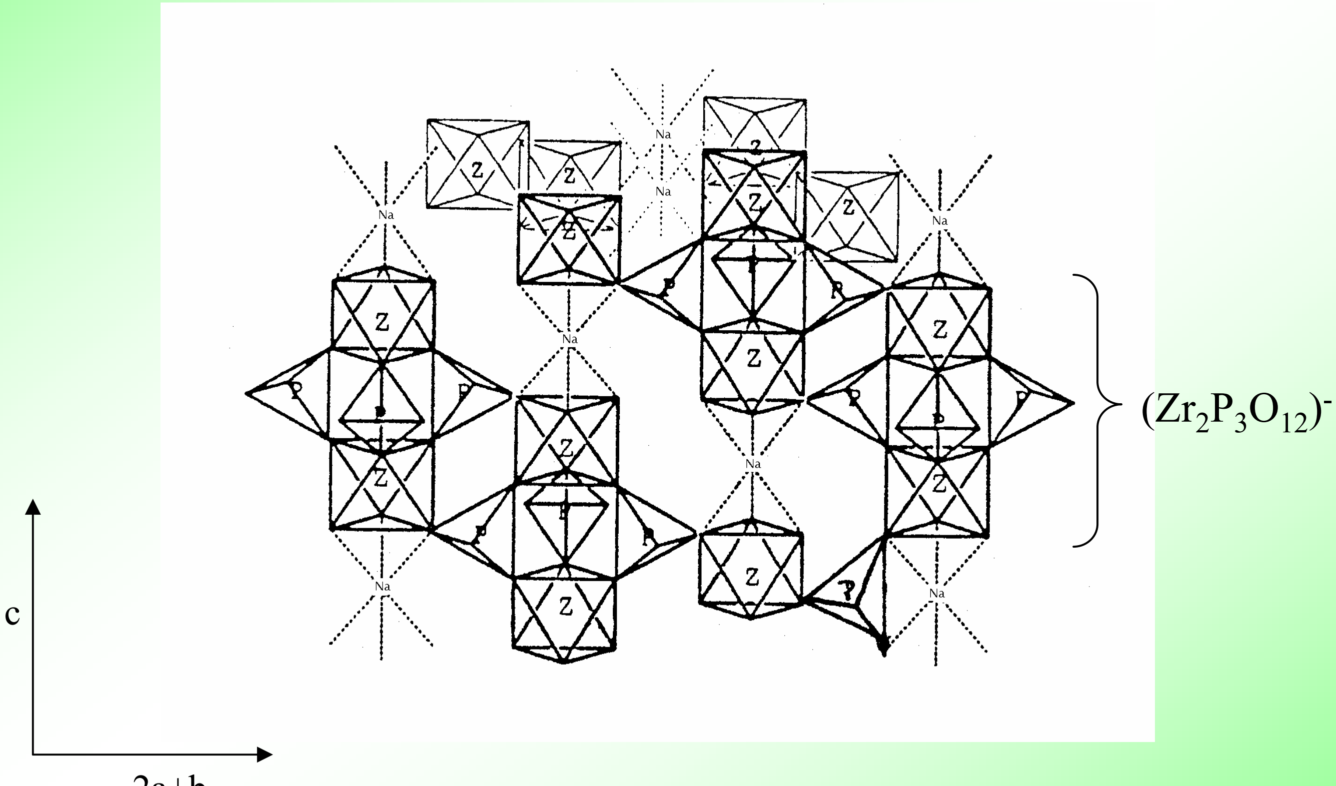


Anisotropic Expansion

$NaZr_2(PO_4)_3$: $\alpha_c = 25.5 \times 10^{-6}\ K^{-1}$; $\alpha_a = -6.42 \times 10^{-6}\ K^{-1}$

Compound	$\alpha_{av} \times 10^6$
$NaZr_2(PO_4)_3$:	4.0
$KZr_2(PO_4)_3$:	0.0
$CaZr_4(PO_4)_6$:	2.6
$(Ca_{0.5}Sr_{0.5})Zr_4(PO_4)_6$:	-0.1

Crystal Structure of NZP



Rhombohedral $R\bar{3}c$

Ionic Substitutions

$$NZP = NaZr_2(PO_4)_3 = Na[\ ]Zr_2\,P_3O_{12}$$

$$[M'][M''][A_2^{IV}][B_3^{V}]O_{12}$$

M-sites: Li, Na, K, Rb, Cs, Ag, H, Mg, Ca, Sr, Ba, Cu

A-sites: Zr, Ti, Sn, Nb, Cr

B-sites: P, Si

Applications

Hot Gas Filters

Removal of particulate matter from hot gas produced by coal gasification or combustion. This protects the turbines downstream from oxidizing, sulfidizing and carburizing environments.

Ceramics	**Metals**
•High Temperature stability	•Mechanical Reliability
•Corrosion Resistance	

NZP

Applications-II

- Catalytic Supports
- Interpenetrating Composites
- Biomedical Components
- Thermal Insulators
- Kiln Furniture

Processing of NZP Ceramics

Low Temperature Casting: Lynch et al., J. Mat. Sci. (1999)

Gel Casting to make Ceramic Foams: Binner et al., Mat. World (2002)

Sol-Gel: Adair et al., J. Am. Ceram. Soc. (1990)

Combustion Reaction Method: Breval, J. Am. Ceram. Soc. (1998)

Spinodal Decomposition of Glass: Yamamoto et al., J. Am. Ceram. Soc. (1997, 1998).

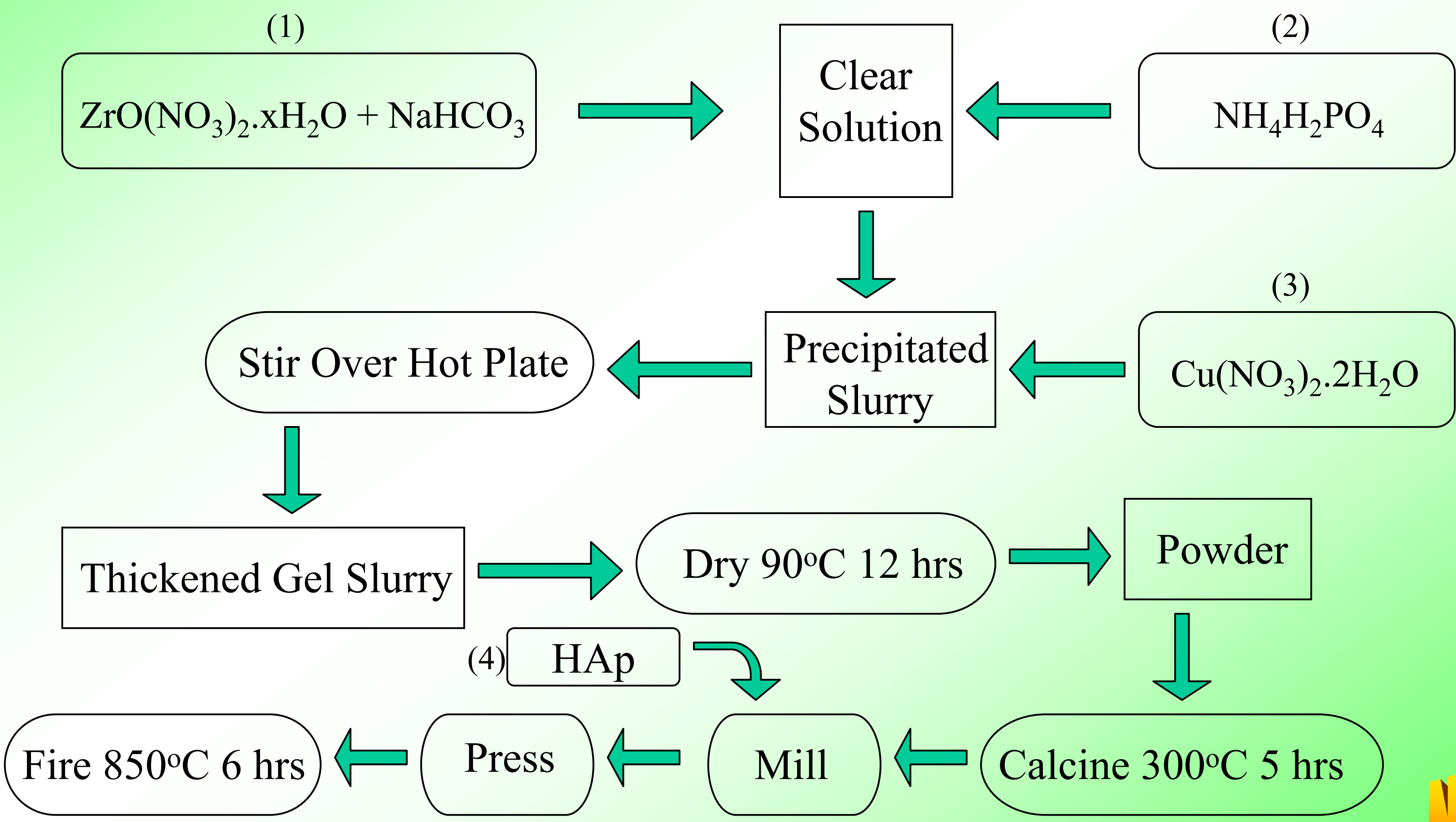
$5CuO.2TiO_2.3P_2O_5$ Glass

Melt at 1250°C, Heat Treat at 520-550°C

Acid Leach with H_2SO_4 or HCl: SA = 45 – 70m^2/g

Experimental Methods

( ) order of mixing

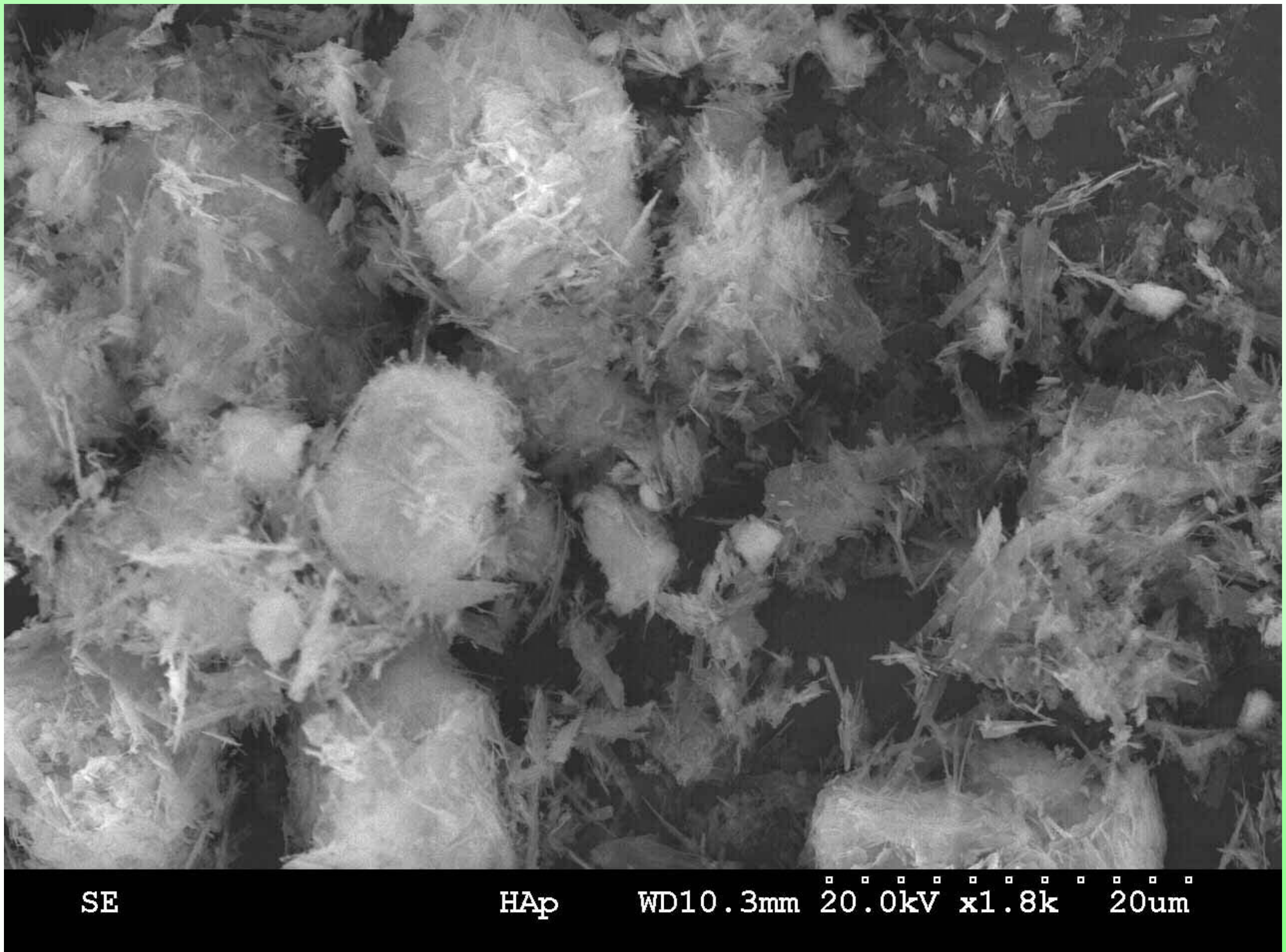


CuO as a sintering aid

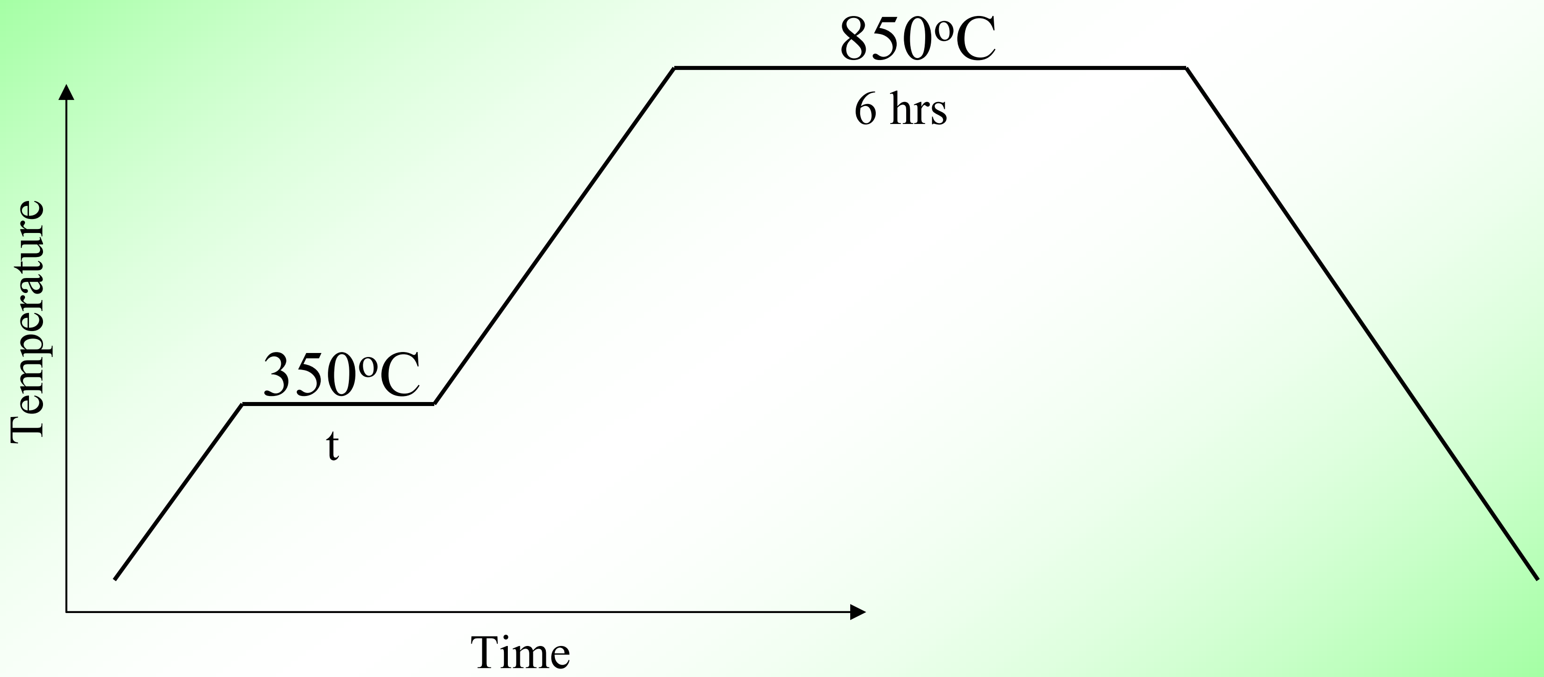
a) 5 wt% CuO	$ZnNb_2O_6$
b) 1 mol% CuO	$BaTiO_3$
c) CuO	TiO_2 and ZrO_2

a) Dong-Wan et al., *J. Am. Ceram. Soc.*, (2001)
b) Derling et al., *J. Mat. Sci.*, (2001)
c) Lu et al., *J. Euro. Ceram. Soc.*, (2001)

HAp: $Ca_5(PO_4)_3OH$

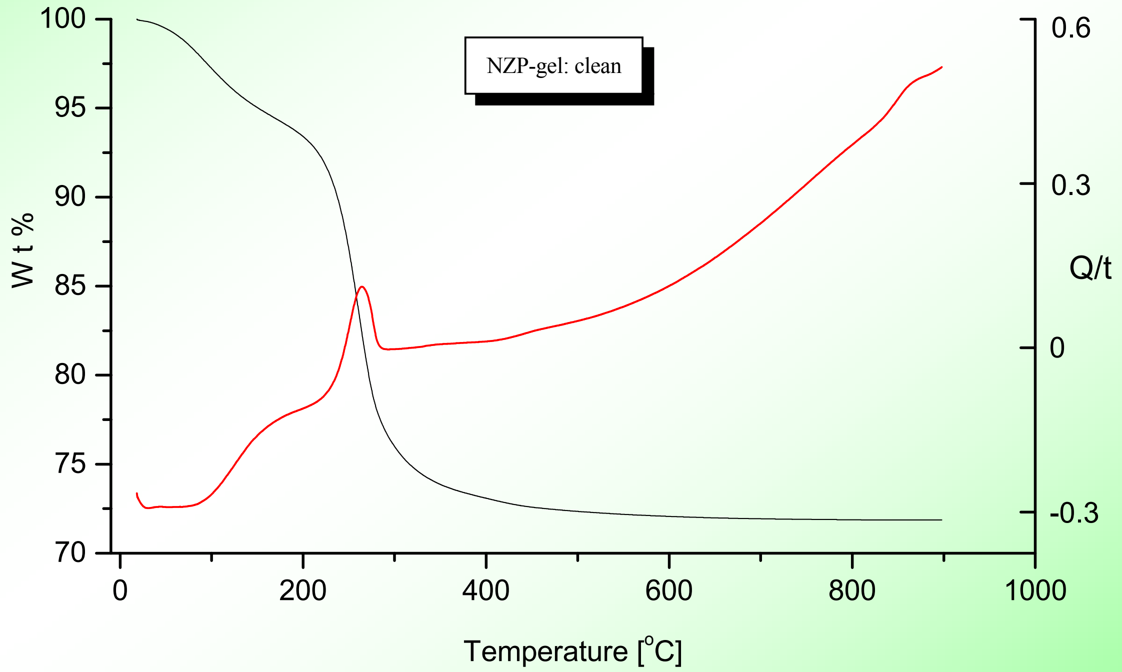


Heating Schedule



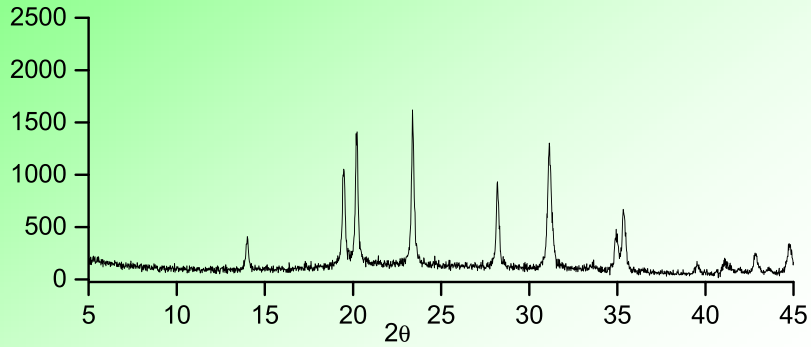
t = 0 - 4 hrs

TGA/DTA

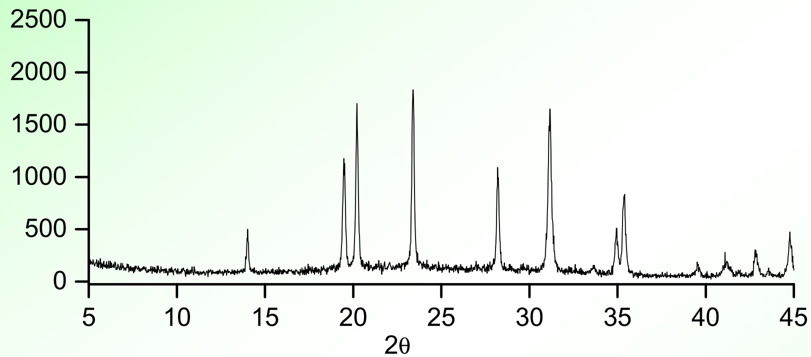


100
95
90
85
80
75
70
W t %
0.6
0.3
0
-0.3
Q/t
NZP-gel: clean
0
200
400
600
800
1000
Temperature [°C]

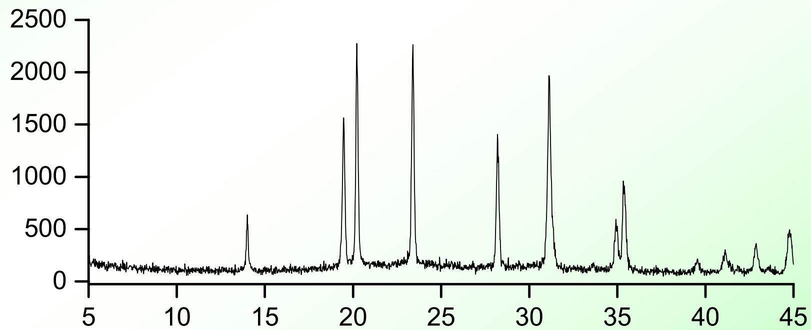
XRD



No additive



10% HAp



5% CuO

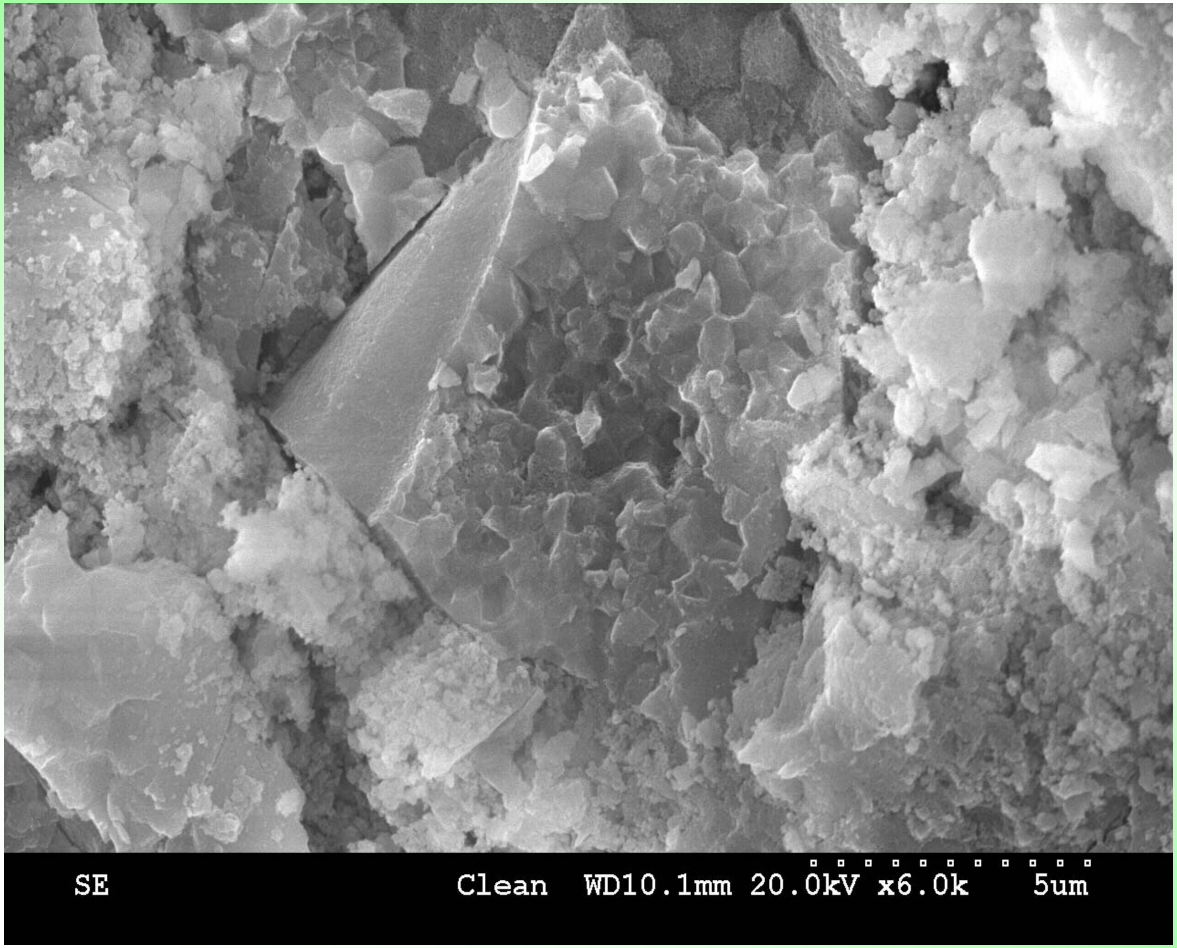
Volume Shrinkage

Color	Composition	ΔVol [%]
	No additives	27
	5% HAp	24
	10% HAp	25
	1% CuO	24
	1% CuO, 5% HAp	31
	2% CuO, 5% HAp	35
	5% CuO	39
	5% CuO, 5%HAp	40

Surface Area (BET)

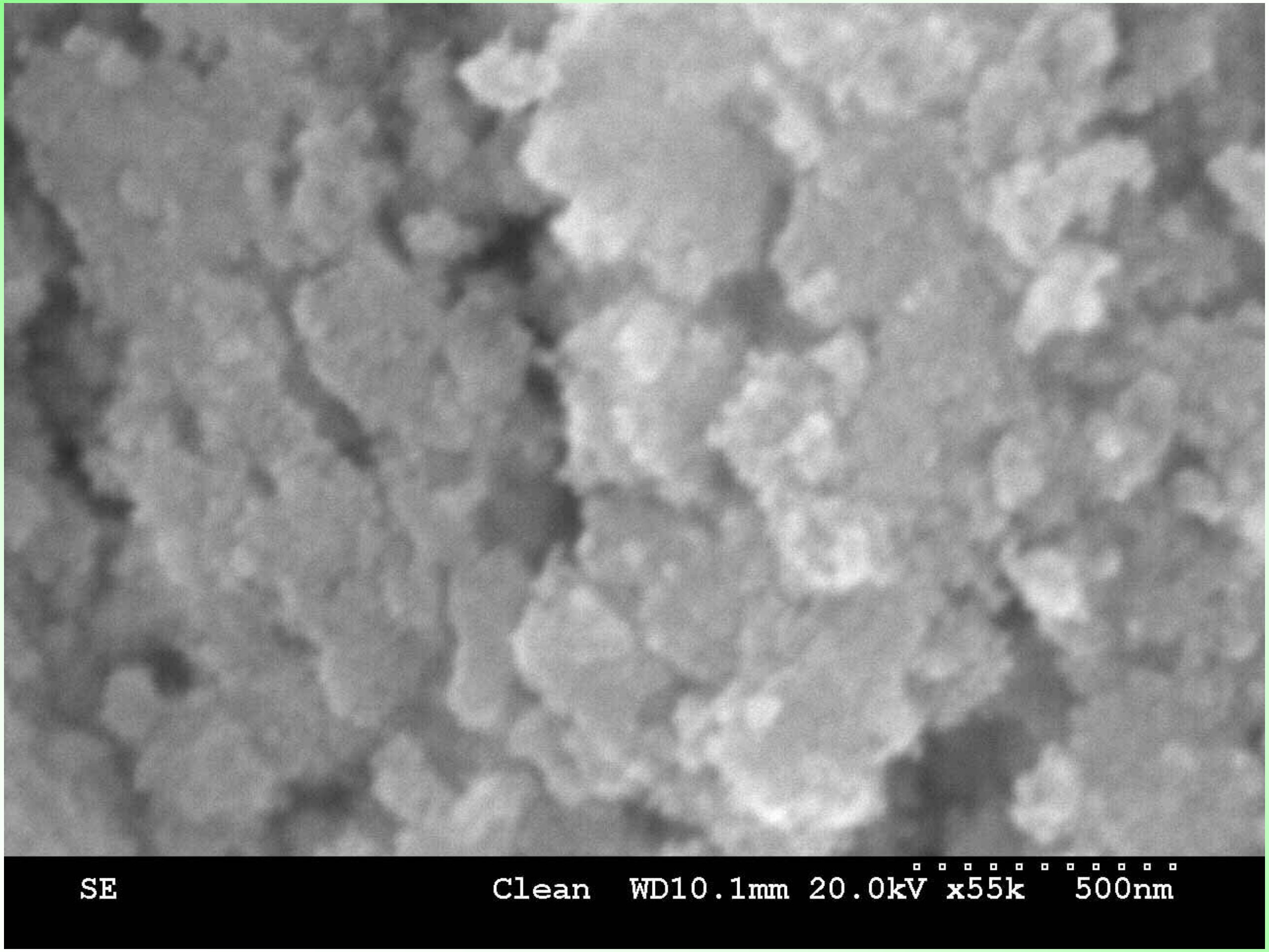
Composition	S.A. [m^2/g]
No additives	30
2% HAp	17
5% HAp	11
10% HAp	5
1% CuO, 2% HAp	14
1% CuO, 5% HAp	6
2% CuO, 5% HAp	5

Morphology (SEM)



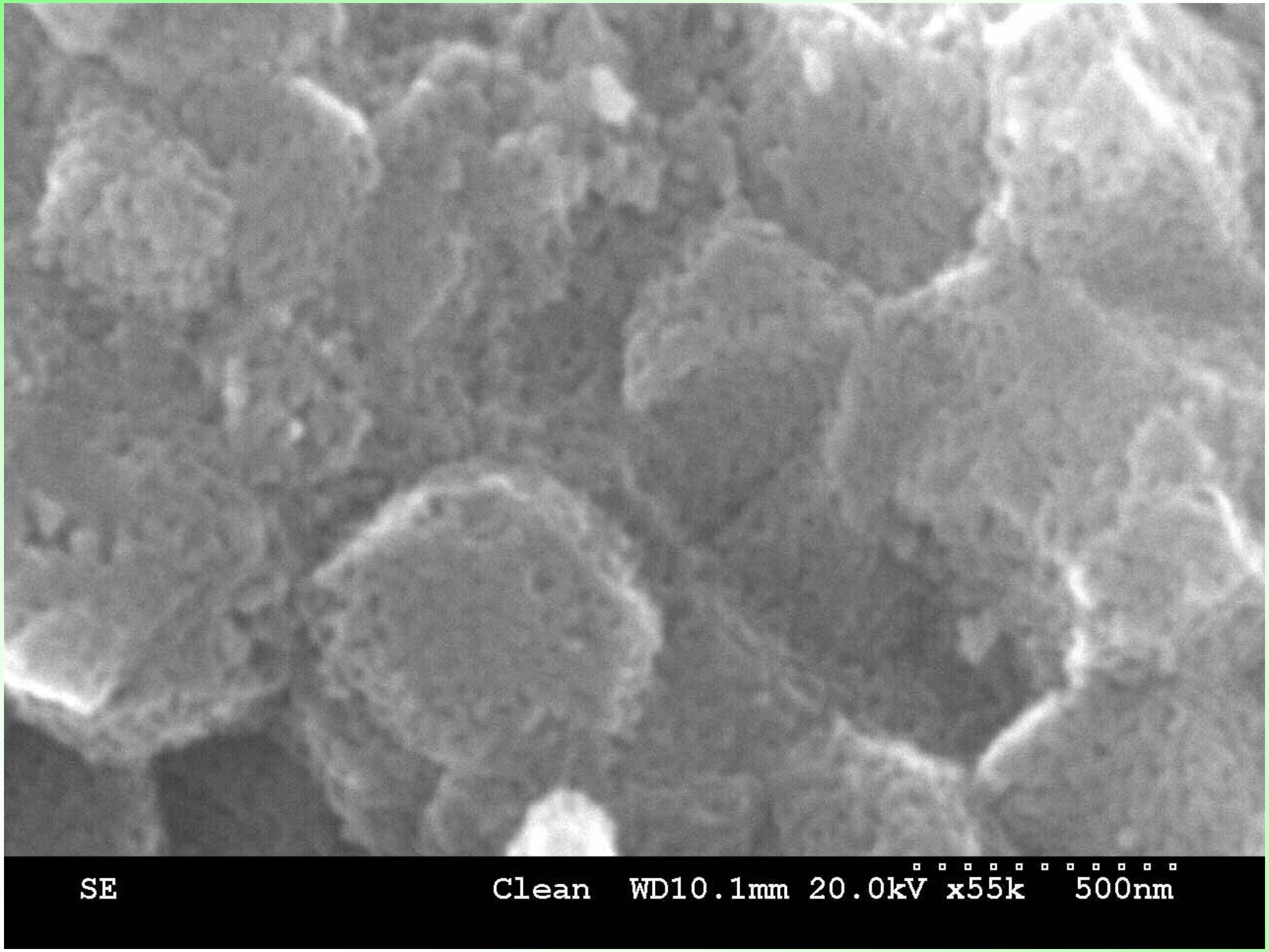
No additive

(a)

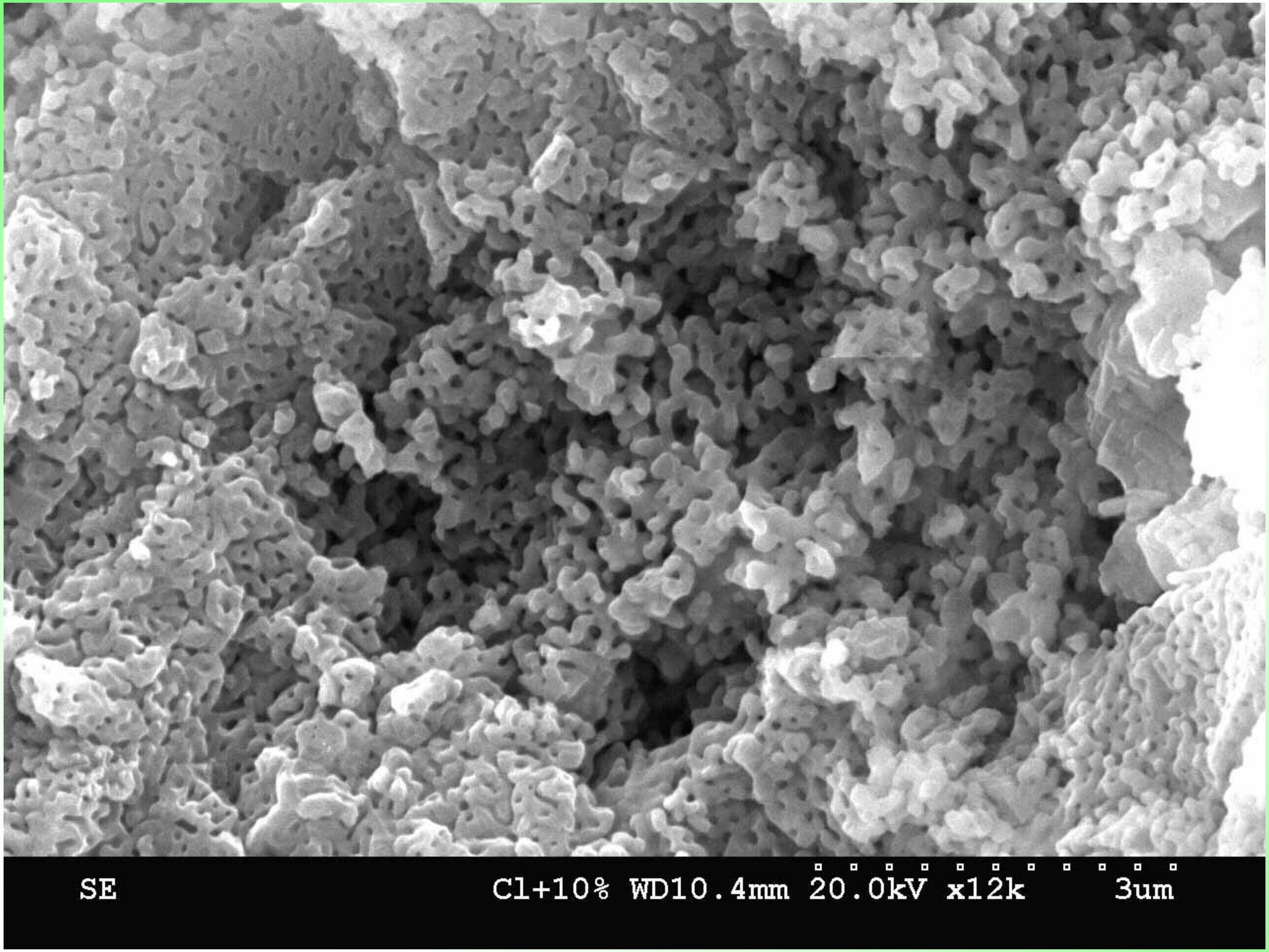


No additive

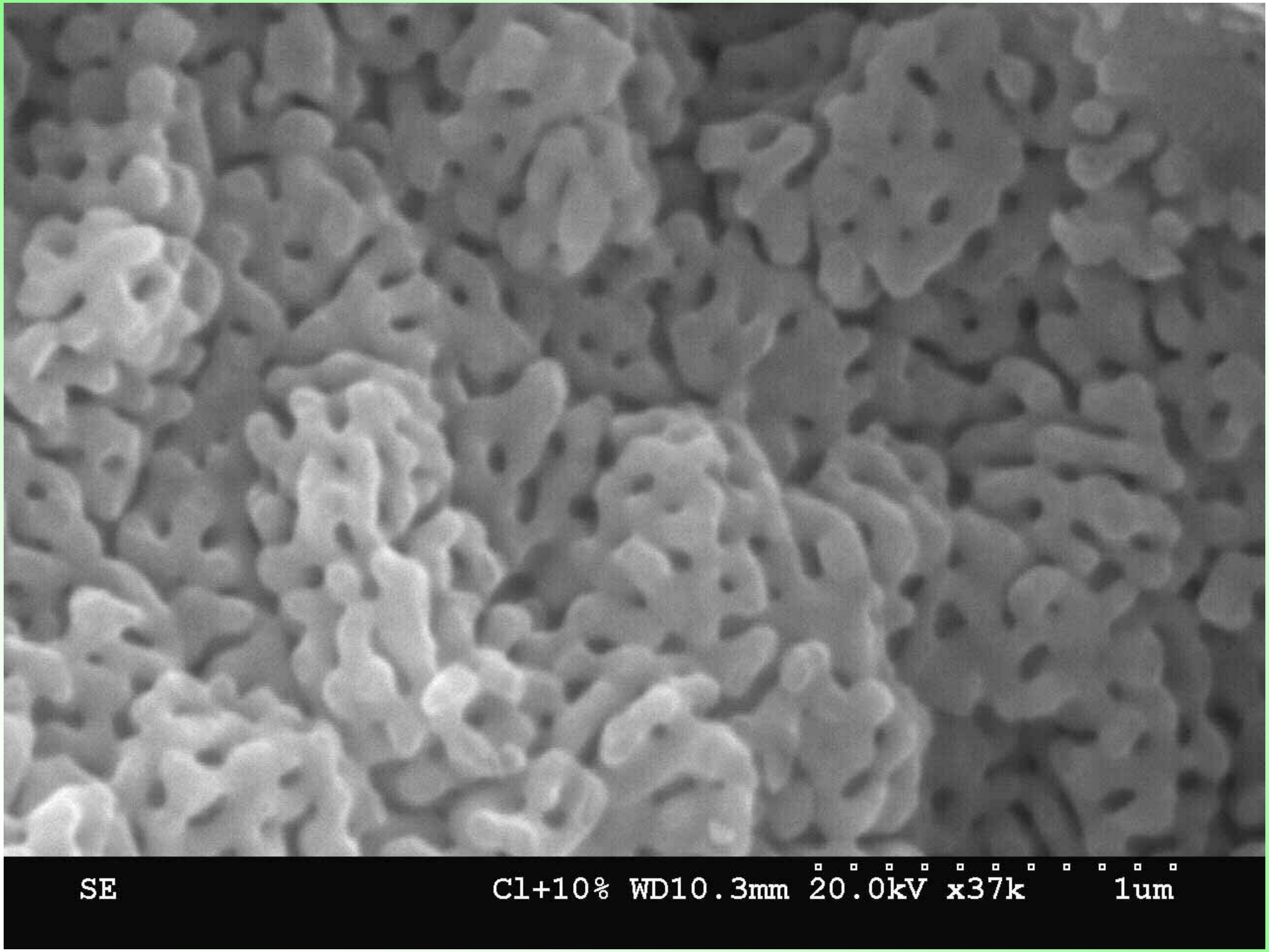
(b)



No additive (c)



10%
HAp
(a)

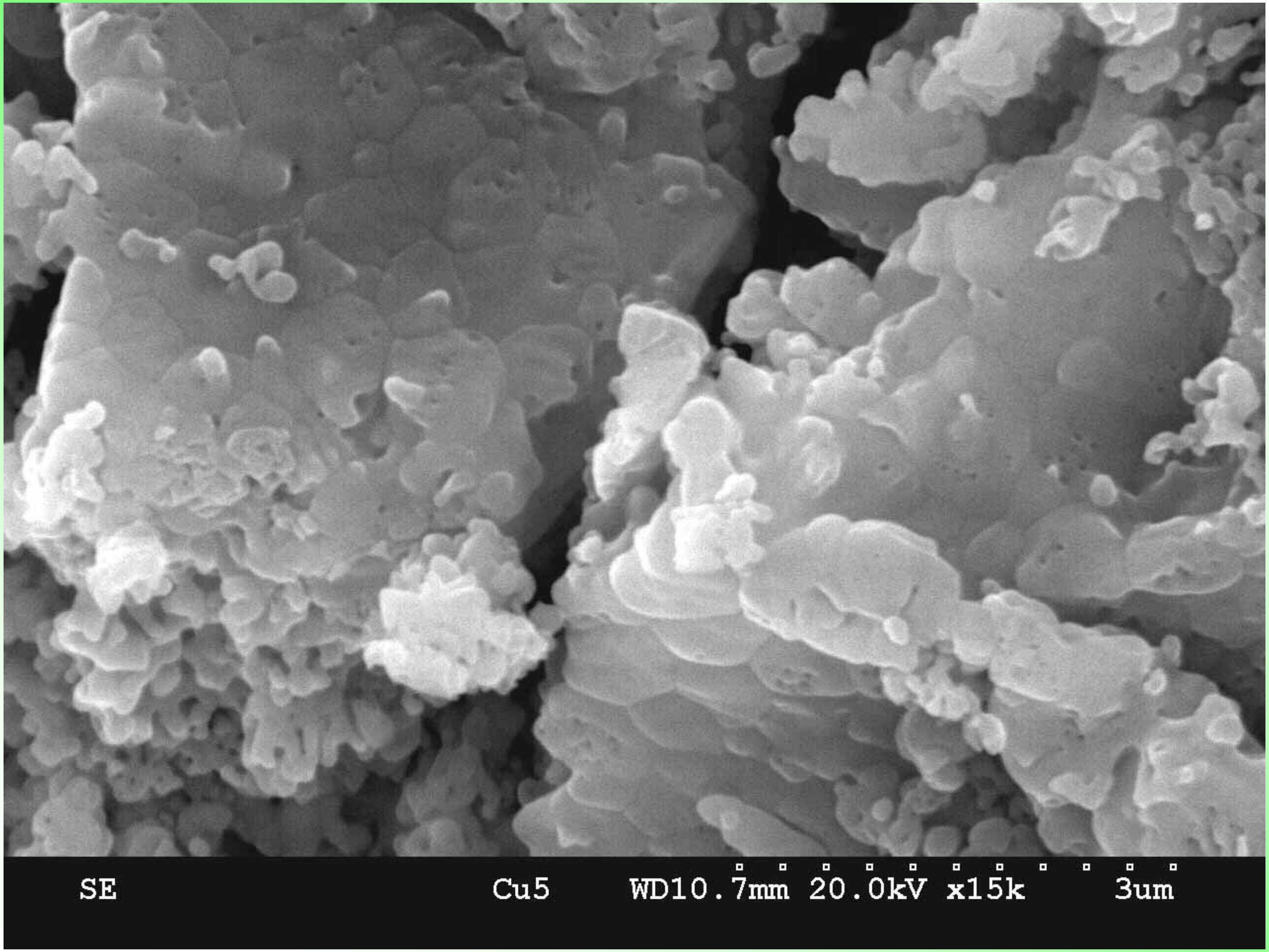


10%
HAp
(b)

CuO

5%

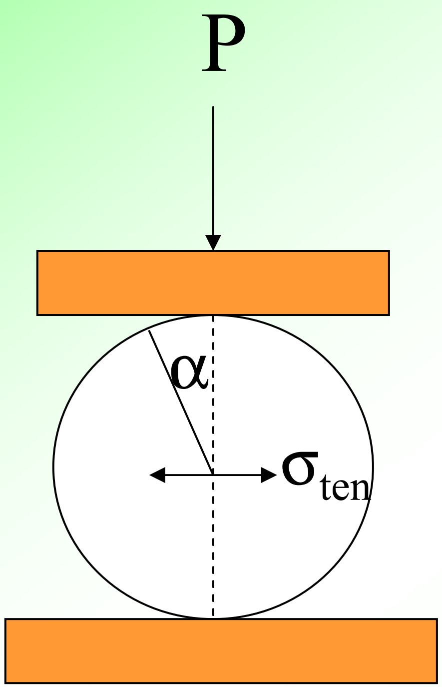
(a)

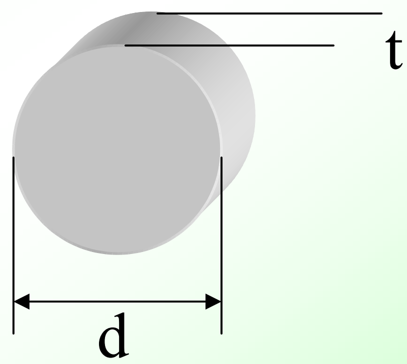


CuO
5%
(b)

Mechanical Properties

$$\sigma_{ten} = \frac{2P}{\pi d t} \times \frac{(\sin 2\alpha - \alpha)}{\alpha}$$





d = 12.8mm

t = 4.5-5mm

Diametral Compression Test

Mechanical Properties (cont.)

Composition	Tensile Strength [MPa]
No additives	8.2
2% HAp	7.8
5% HAp	8.6
10% HAp	9.9
1% CuO, 5% HAp	11.6
2% CuO, 5% HA	13.5
5% CuO	14.9
5% CuO, 5% HAp	16.8

Conclusions - NZP

- Phase-Pure NZP 850^{o}C
- High Surface Area (30m^2/g)
- Unique 3-D Interconnected Pore-structure
- Tensile Strengths up to 16 MPa
- Strength ↑ Surface Area ↓
- Strength ↑ Shrinkage ↑

NASICON

Na Super Ionic Conductor

$Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$

$ZrO(NO_3)_2.xH_2O$
$+ NaHCO_3$
$+ NH_4H_2PO_4$

→

X = 2

Slurry

←

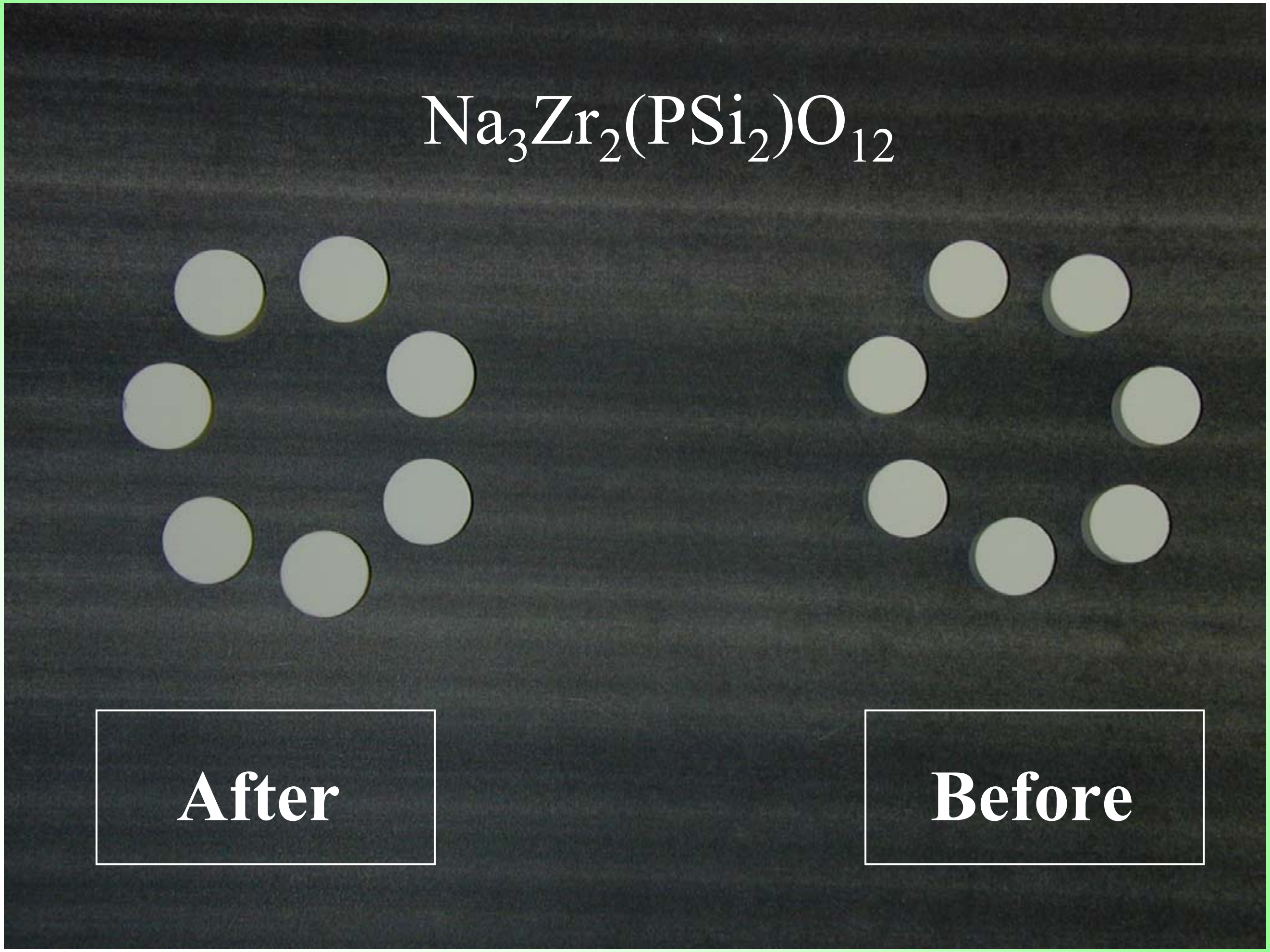
Ppt'ed. Amorphous SiO_2

Anionic Surfactant

Calcine 700°C 7 hr → Fire 1100°C 6 hr

NZP

Expansion!! with sintering



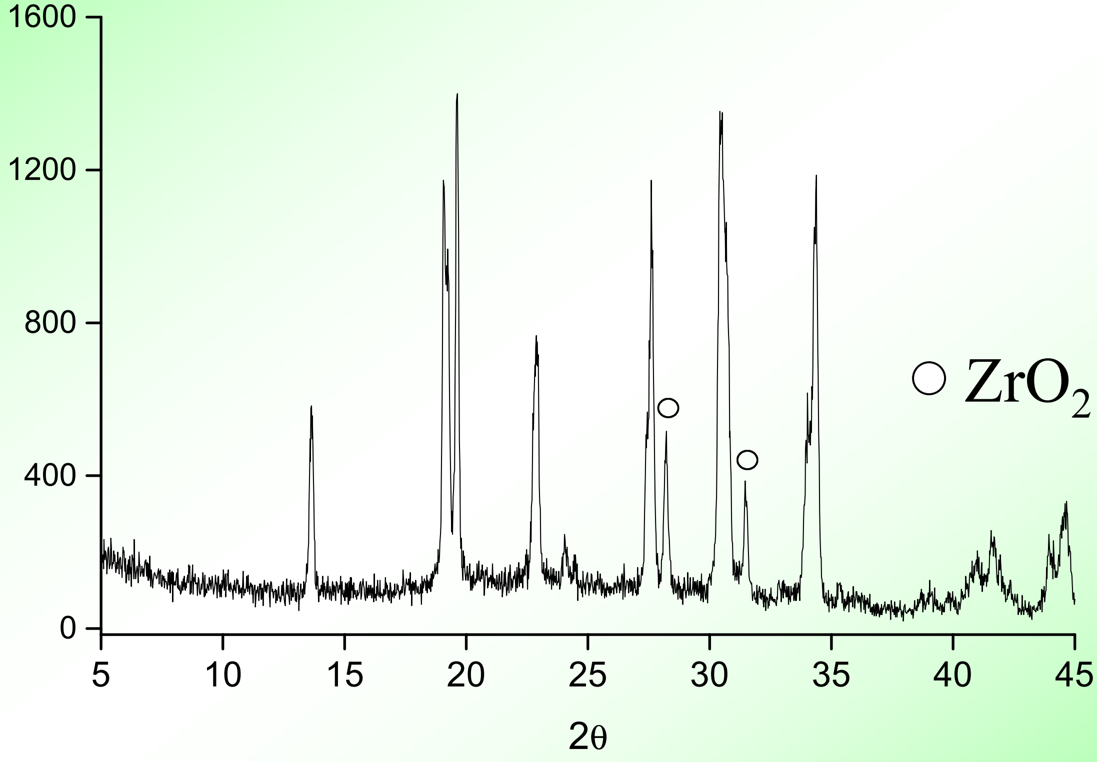
Volume Change

Composition	ΔVol%
No additives	+ 24
1% CuO	+ 16.5

Surface Area (BET)

Composition	S.A. [m^2/g]
No additives	0.81
1% CuO	0.41

XRD



$Na_3Zr_2(PSi_2)O_{12}$

Processing of Nasicon

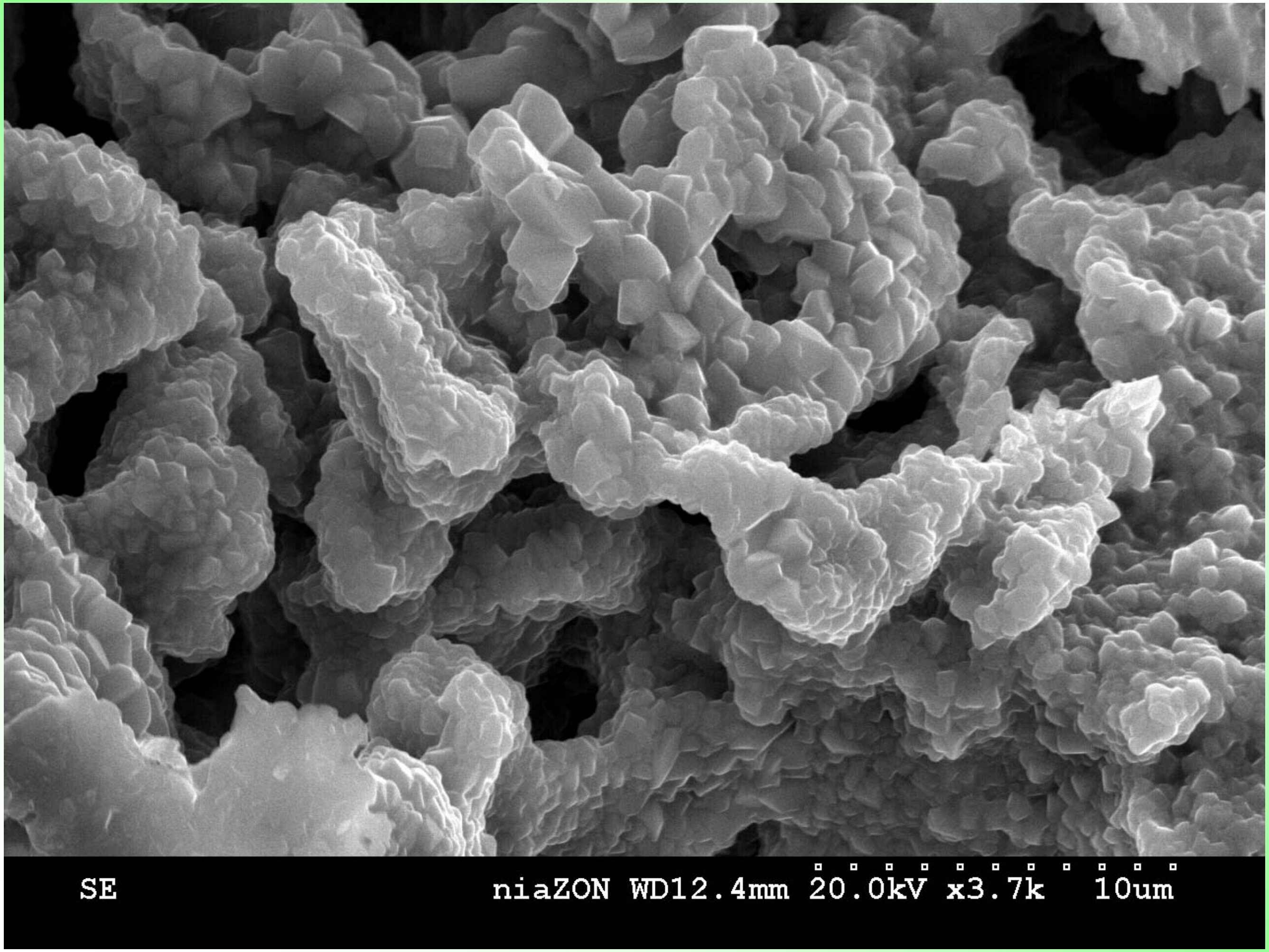
Difficult to form Phase-Pure Nasicon

ZrO_2 Always Present

Liquid Phase: 1320 to 1260^{o}C

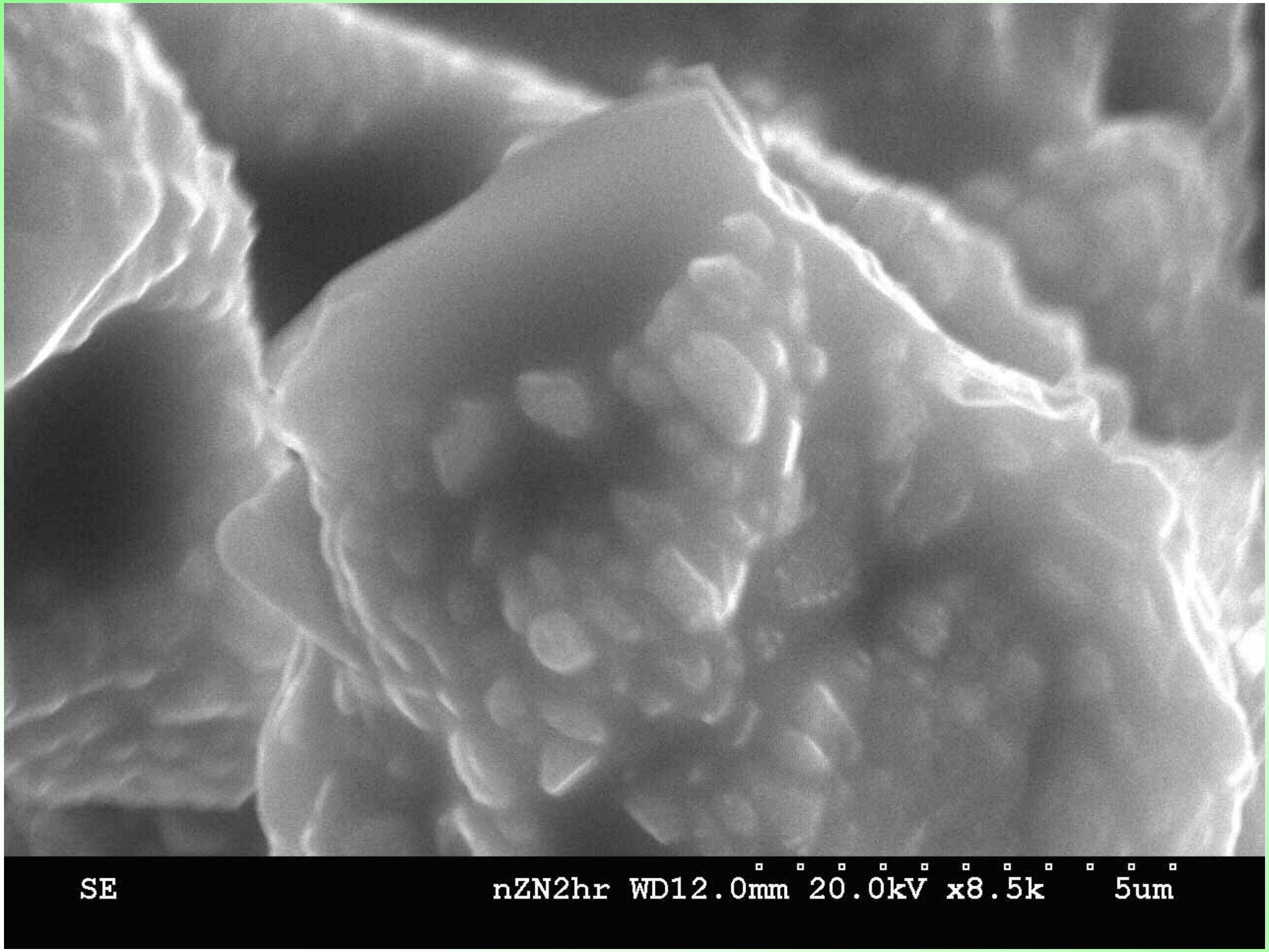
Kang and Cho, *J. Mat. Sci*, (1999)

Microstructure (SEM)



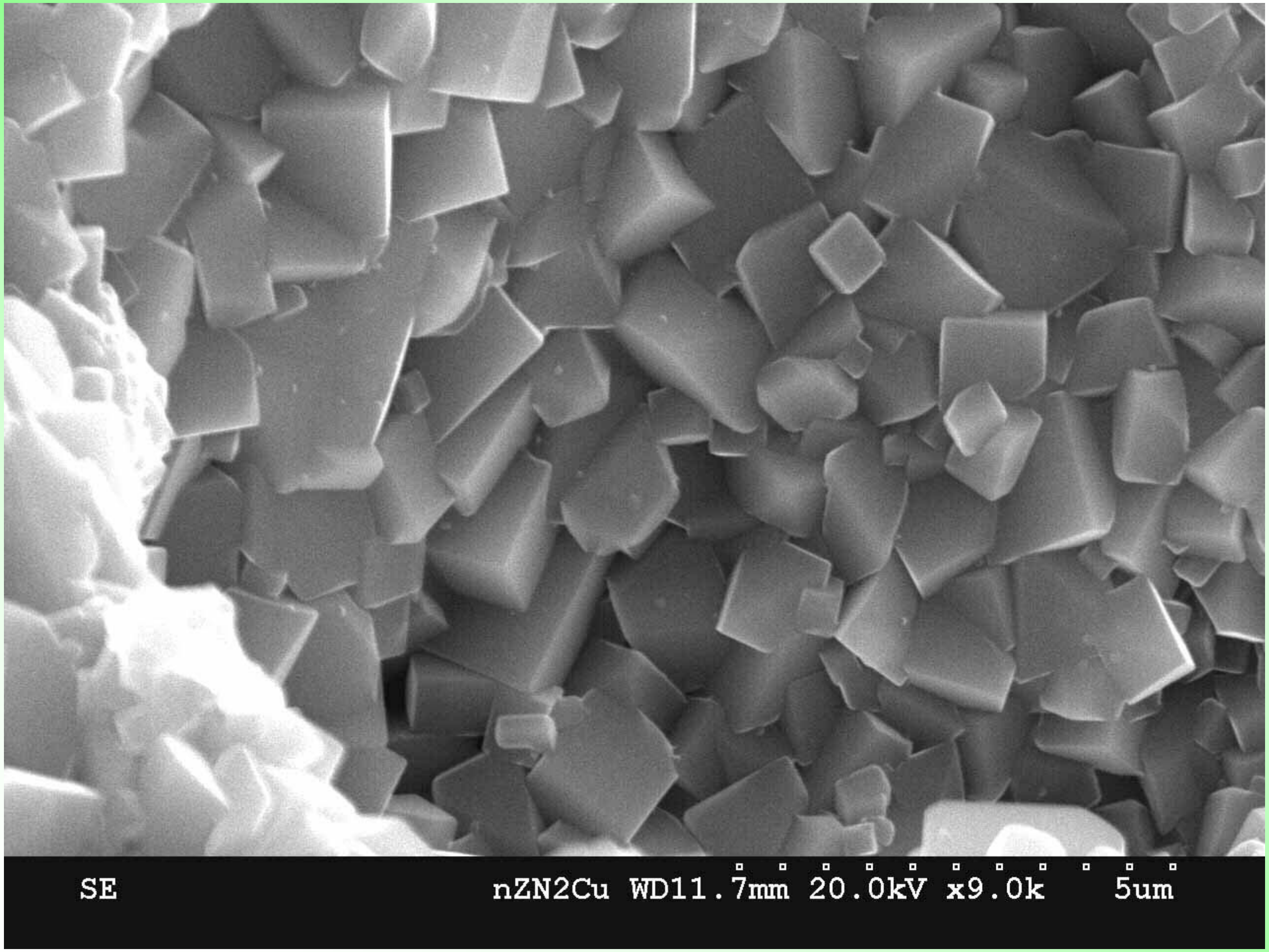
No additives 6 hr

SEM



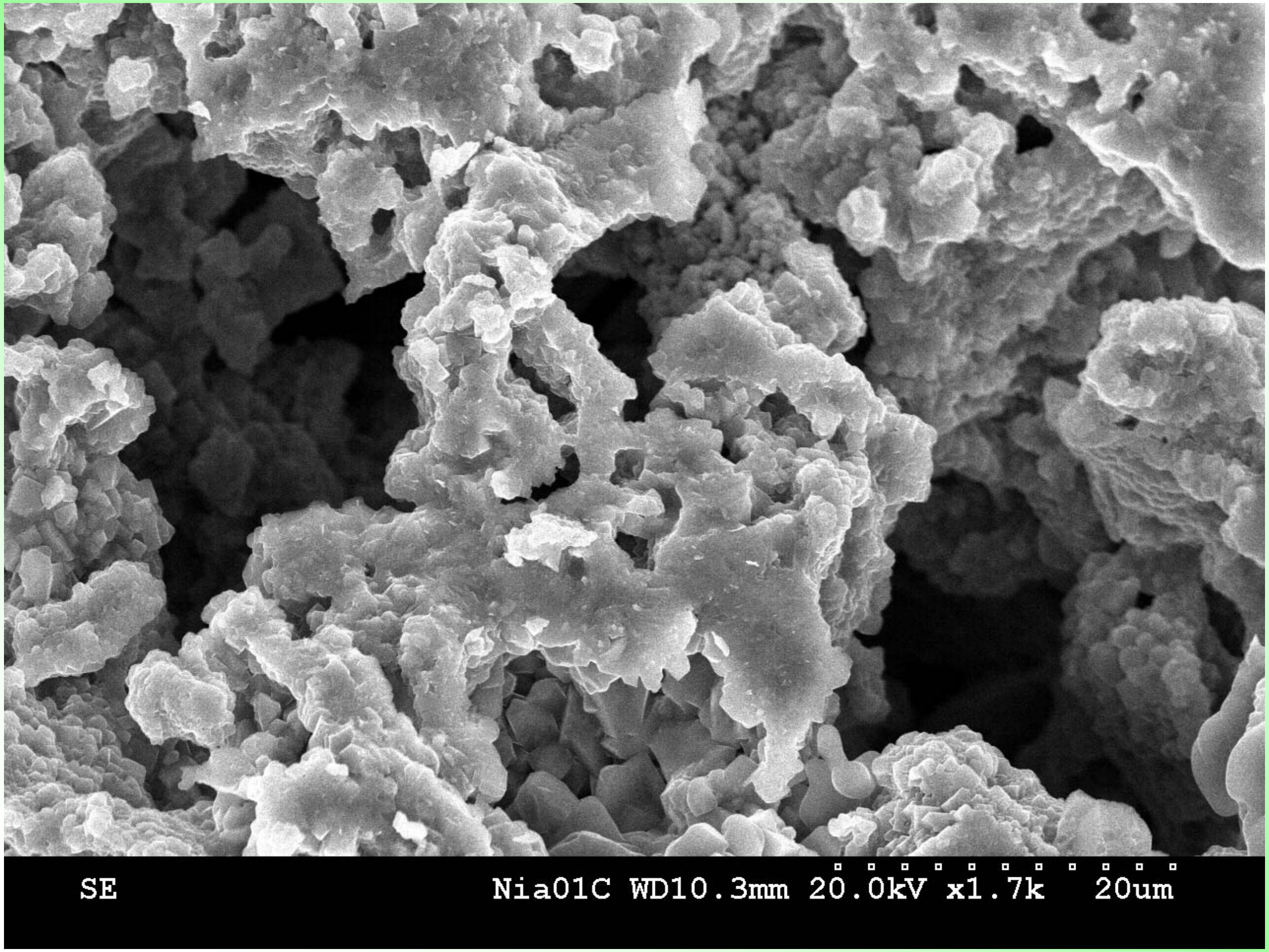
No additives
2 hr

SEM



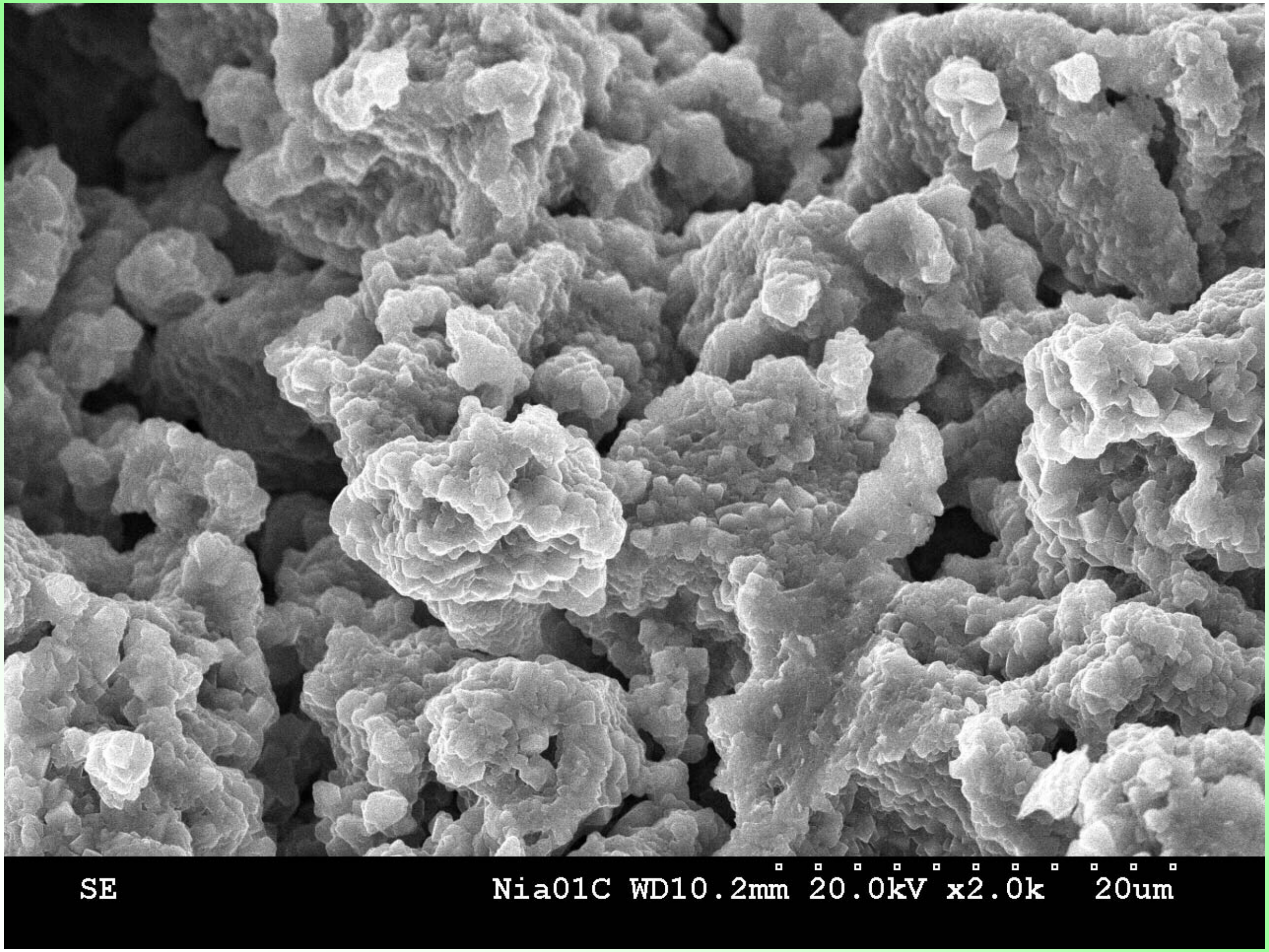
1% CuO
2 hr

SEM



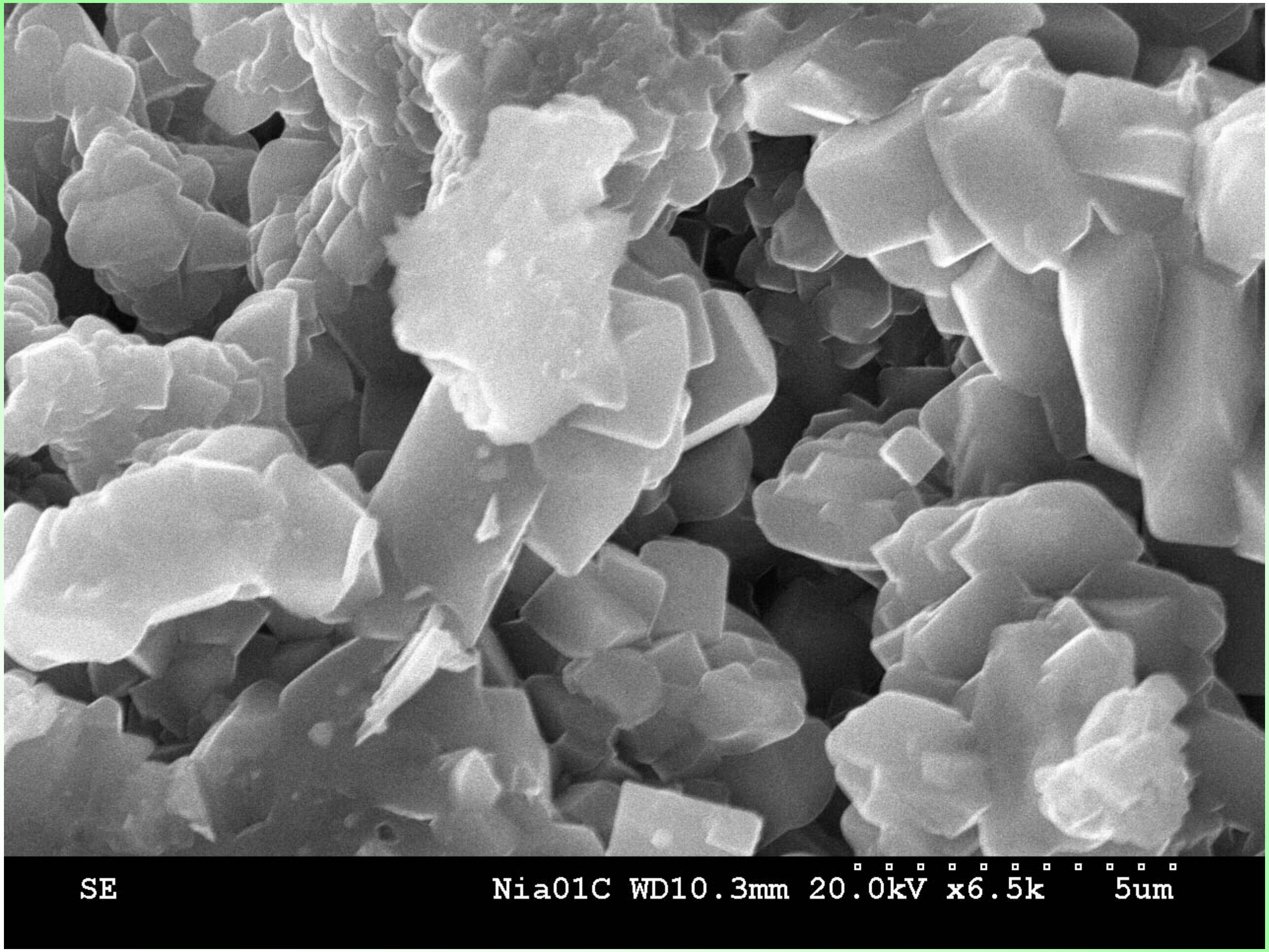
1% CuO
6 hr

SEM



1% CuO
6 hr

SEM



1% CuO
6 hr

Conclusions- NASICON

- Nasicon Formation at 1100°C
- Large Crystals
- Expansion with firing
- Open Pore Structure

Future Work

- Correlation: Processing and Properties
- Interpenetrating Composites
- Near Net Shape Processing (Nasicon)

Publications

- *Low-temperature formation of NZP ceramics*, Journal of the American Ceramic Society, submitted.
- *Effect of CuO on NASICON formation*, Journal of Materials Science, submitted.