

Summer 6-26-2005

XII, Part 2: Novel properties of glass-metal nanocomposites

D Chakravorty

Indian Association for the Cultivation of Science

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NOVEL PROPERTIES OF GLASS-METAL NANOCOMPOSITES

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Acknowledgment:

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S.Bhattacharya, Supriya Chakraborty

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OUTLINE

- Glass-Ceramics \longrightarrow Template for nano metal growth.
- Silver nanowires in gel derived silica glass \longrightarrow Single electron tunneling
- Silver nanowires in fluorophlogopite mica glass-ceramics \longrightarrow Giant dielectric permittivity
- Metal core-metal oxide shell nanostructure in silica glass \longrightarrow Interfacial amorphous phase
- Glass-Ceramic- metal nanocomposites \longrightarrow Large Relative Humidity Sensitivity
- Silicate glass with nano metal arrays \longrightarrow Diode- like behaviour

Growth of Nanocrystalline Metal at Glass-Crystal Interface

Glass 55SiO₂ 12ZnO 32.2 Li₂O 0.8P₂O₅

Heat treated

565⁰C / 1 hr.+ 630⁰C/3 hr.

Glass- Crystal Composites

Zn₂SiO₄ + Li₄P₂O₇ : Crystalline

phase

Ion Exchange

Li⁺ ⇌ Ag⁺ (Silver Nitrate at 310⁰C/8 hr.)

Li⁺ ⇌ Cu⁺ (CuCl, 510⁰C/3 hr.)

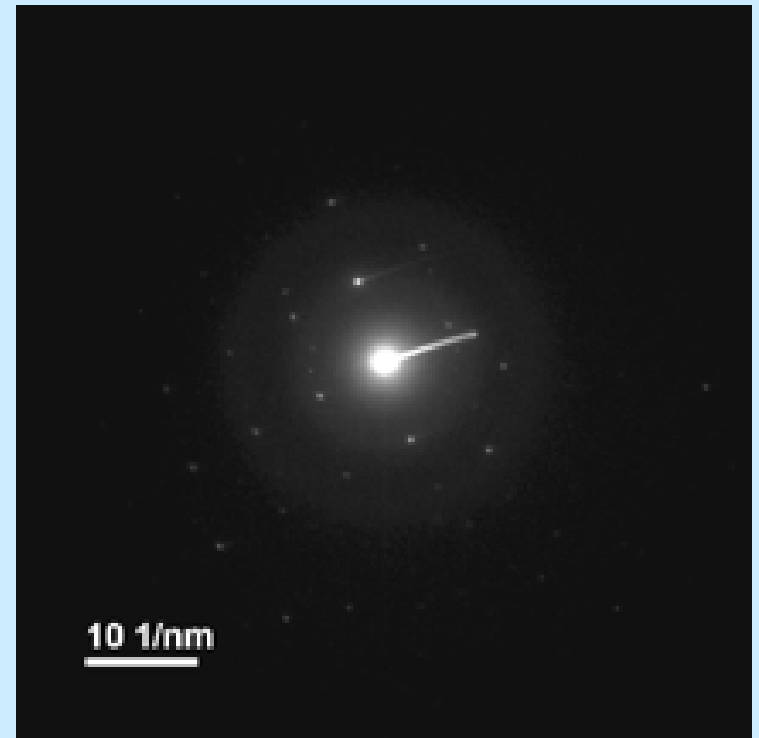
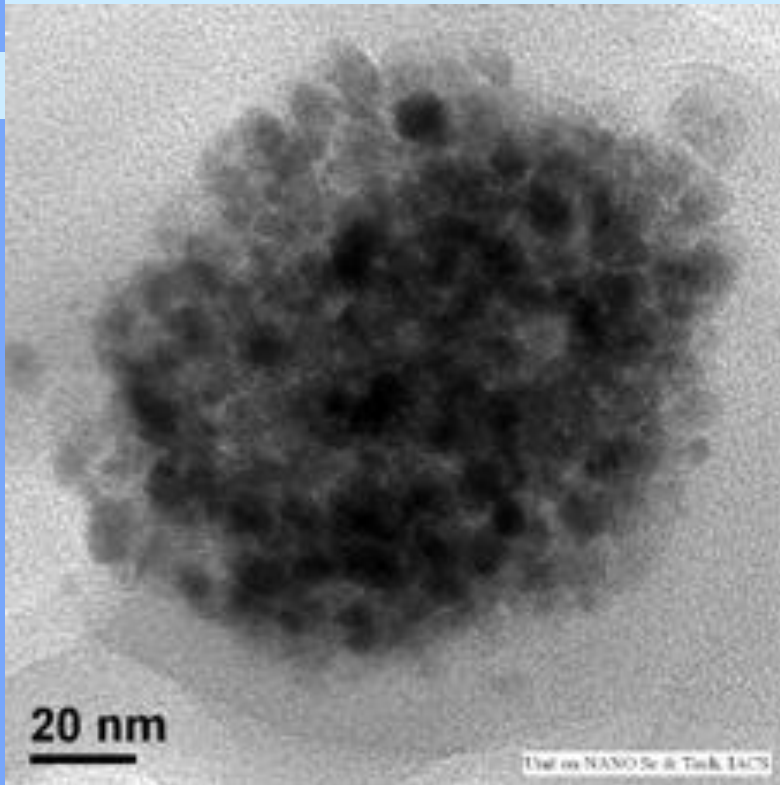
Reducible ion enriched Glass-Crystal Composite Layer

3Li⁺ ⇌ Fe³⁺ (FeCl₃, 300⁰C/50 hr)

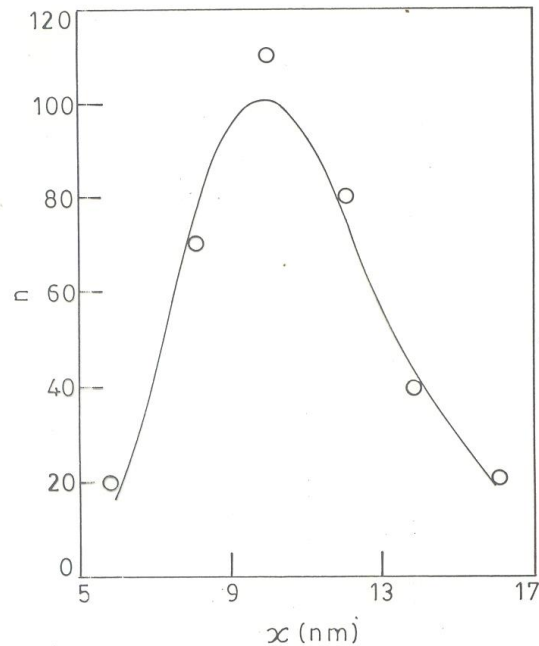
Reduction in H₂

Nanoparticles of Metal at Glass-Crystal Interface

Growth of Nanocrystalline Metal at Glass-Crystal Interface



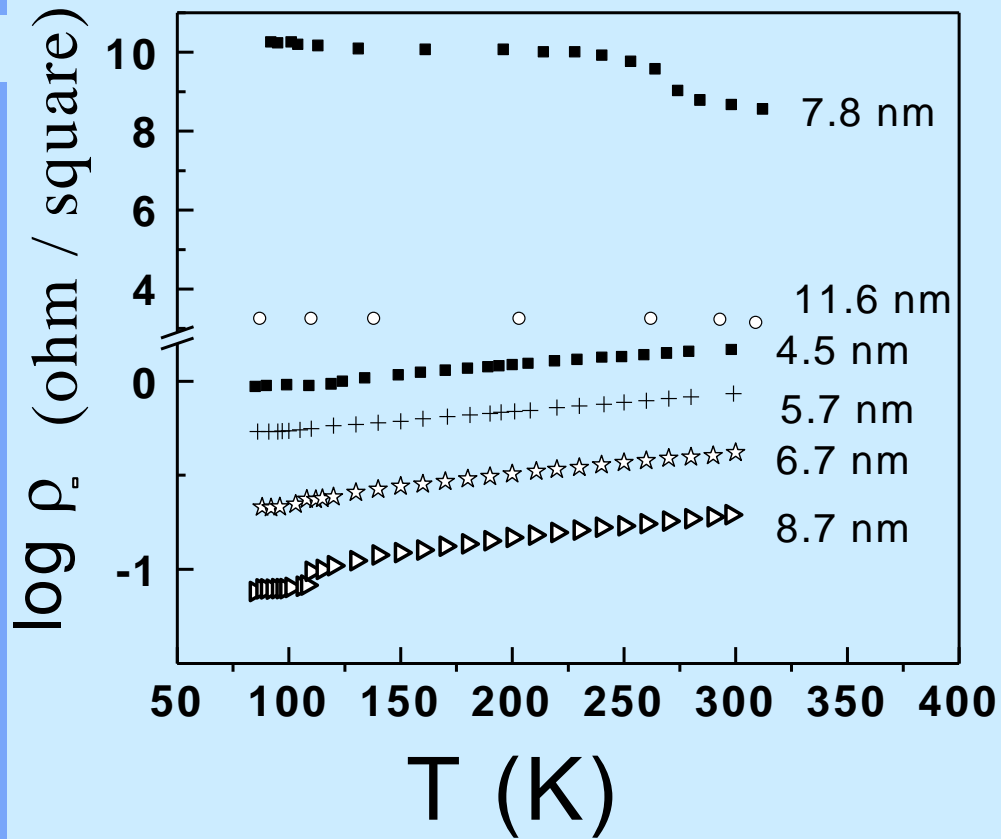
Growth of Nanocrystalline Metal at Glass-Crystal Interface



Size distribution of Silver Particles
Synthesized by ion exchange and
reduction(873K for 1/2 hr) in a glass
of Composition
 $55\text{SiO}_2, 32.2 \text{LiO}_2, 12 \text{ZnO}, 0.8\text{P}_2\text{O}_5$

$$\Delta n = \frac{1}{\sqrt{2\pi} \cdot \ln \sigma} \exp \left\{ -\frac{1}{2} \left(\ln \left(\frac{x}{\bar{x}} \right) / \ln \sigma \right)^2 \right\} \Delta(\ln x)$$

Growth of Nanocrystalline Metal at Glass-Crystal Interface



Growth of Nanocrystalline Metal at Glass-Crystal Interface

Electron Tunnelling between Metal Islands

Neugebauer and Webb model:

$$\rho \propto \exp(2\alpha s + E / kT)$$

α : Tunnelling exponent $(= \left(\frac{2m\phi}{\hbar^2} \right)^{1/2})$

s : Inter-Grain distance

E : Energy to charge a grain

ϕ : Effective barrier height

$$E = \frac{e^2}{2\pi\epsilon\epsilon_0} \left(\frac{1}{r} - \frac{1}{r+s} \right) \quad (\text{Tick and Fehlner 1972})$$

e : electronic charge

r : metal grain radius

ϵ : dielectric constant of matrix

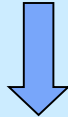
ϵ_0 : dielectric permittivity of free space

NANOWIRES IN SILICA GEL NANOPORES

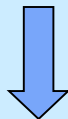
GEL SAMPLES HEAT TREATED AT TEMPERATURES 523 TO 823 K FOR 6 HRS



DIPPED INTO A SOLUTION OF AgNO_3

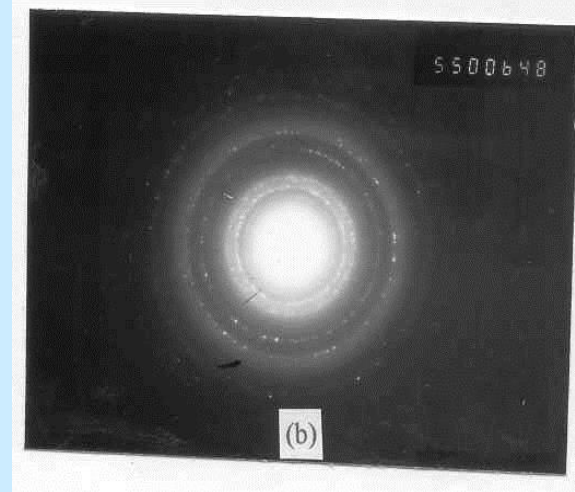
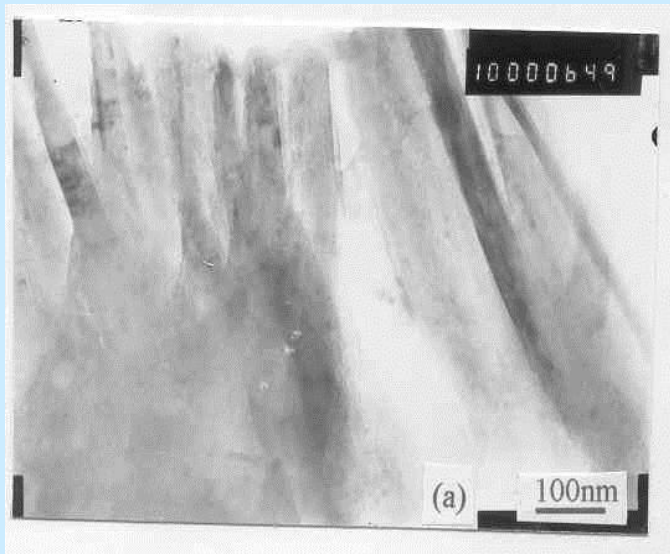


SAMPLES COATED WITH SILVER PASTE ELECTRODES



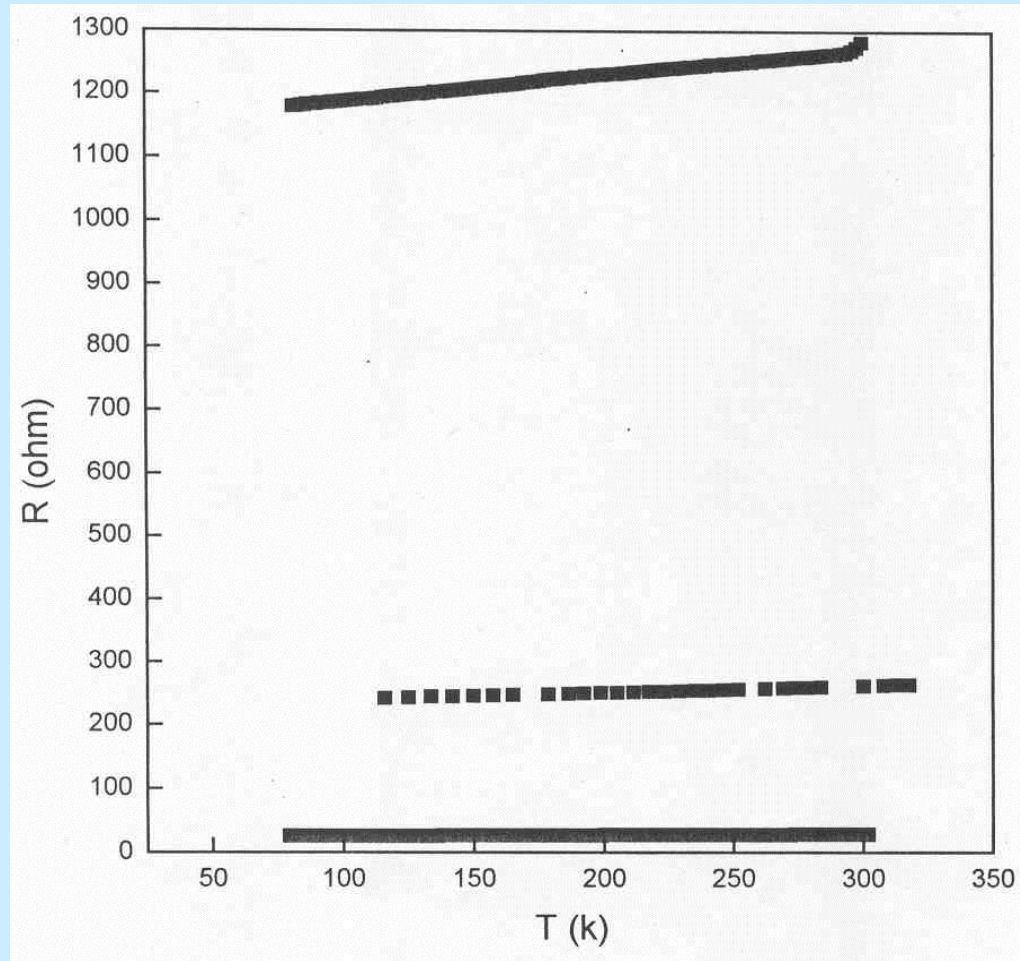
ELECTRODEPOSITION AT 8 VOLTS

SILVER NANOWIRES IN SILICA GEL

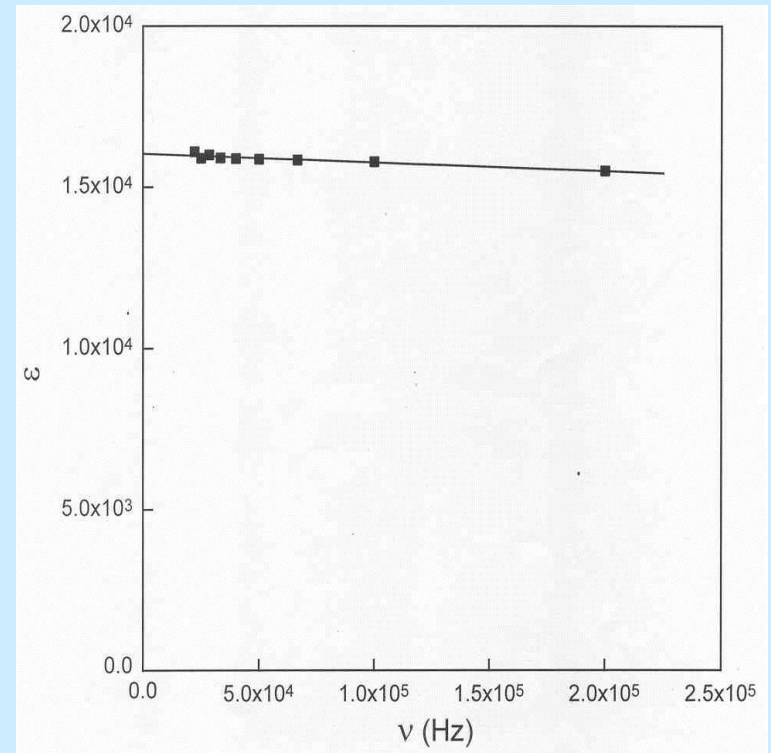
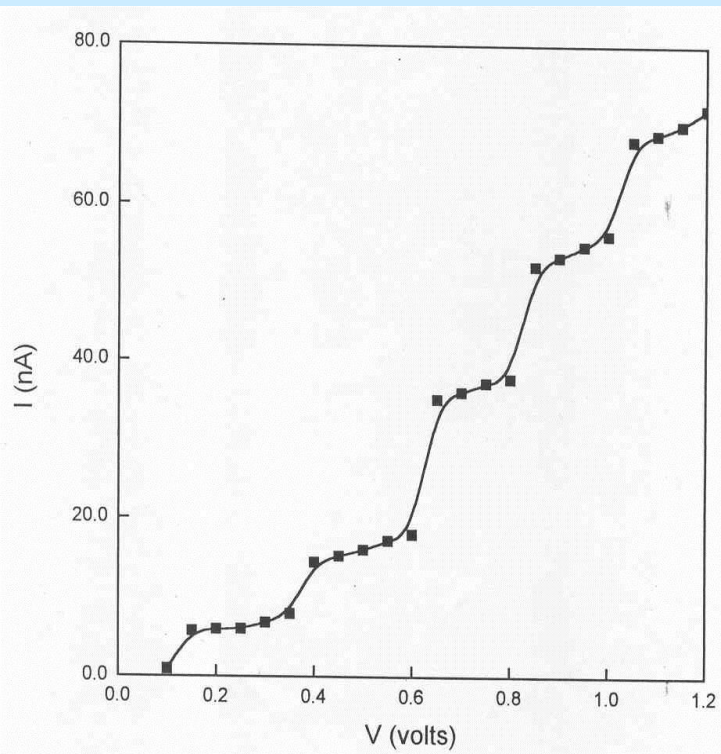


TEM for silica gel heat at 723K/6h.soaked AgNO_3 and
Subjected to electrodeposition

SILVER NANOWIRES IN SILICA GEL



SILVER NANOWIRES WITH BREAK JUNCTION IN SILICA GEL



GROWTH OF SILVER NANOWIRES IN NANO CHANNELS OF FLUOROPHLOGOPITE MICA ($\text{KMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$)

GLASS COMPOSITION (TYPICAL) :

42 SiO_2 15 B_2O_3 9 Al_2O_3 8 MgO 20 K_2O 6 KF



HEAT TREATMENT AT 1168 K FOR 2 HRS



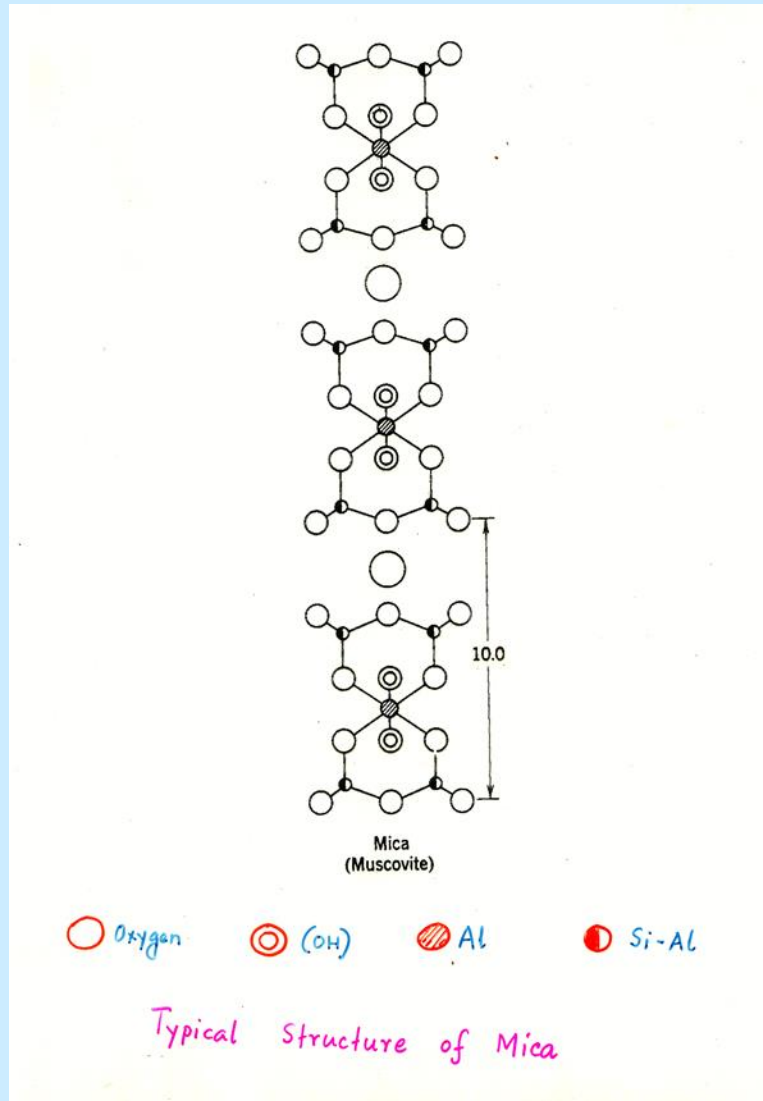
ION EXCHANGED IN AgNO_3 AT 573 K FOR 24 HRS



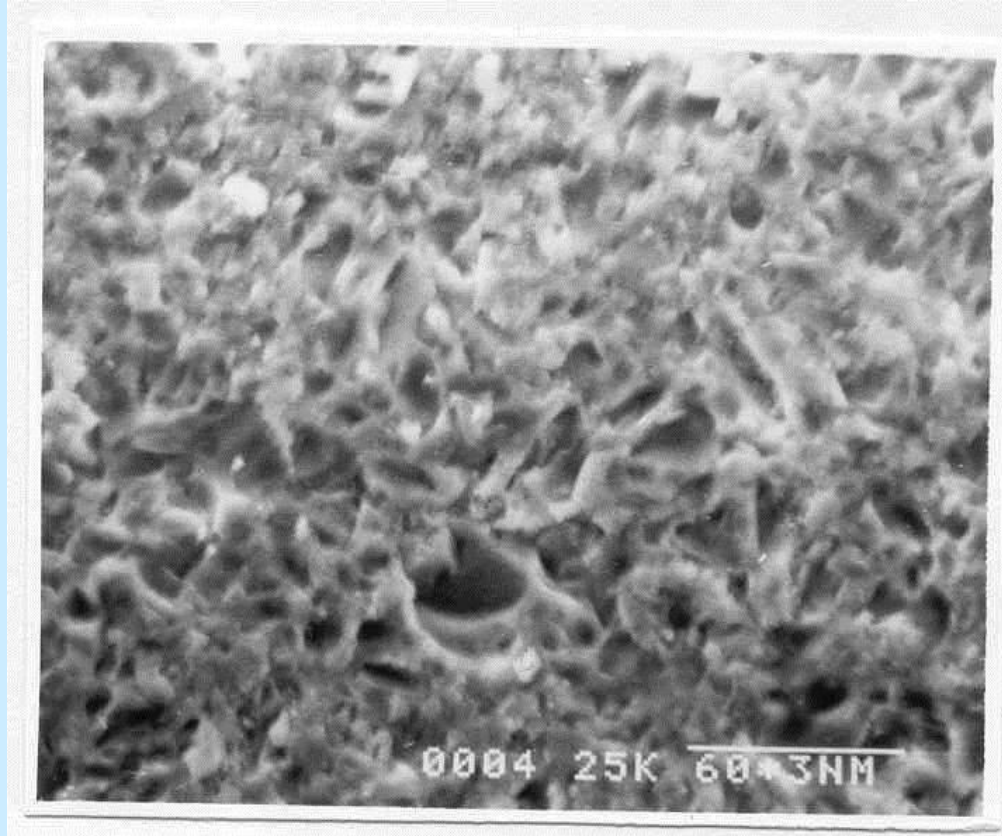
ELECTRODEPOSITION WITH 10 VOLTS AT 370 K
(SILVER PASTE ELECTRODES)

GROWTH OF SILVER NANOWIRES IN NANO CHANNELS OFFLUOROPHLOGOPITE MICA

Crystal Channels as Templates for Growing Nanowires

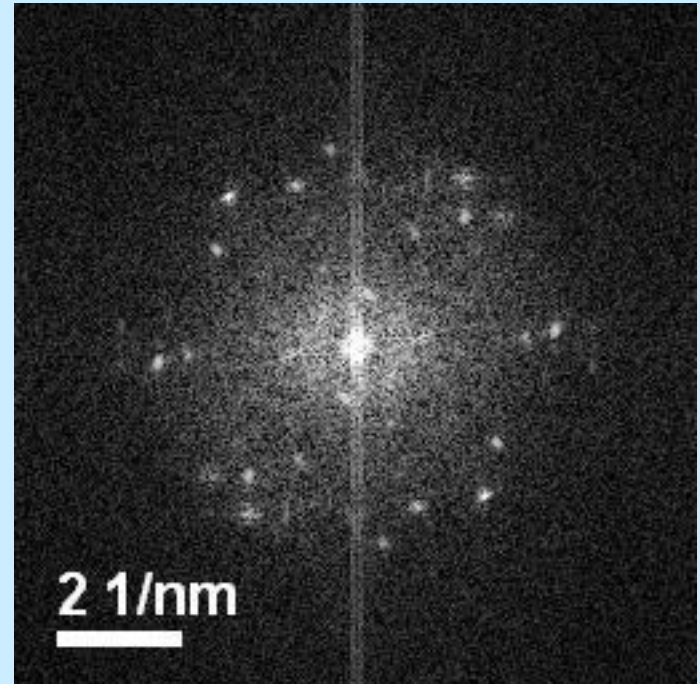
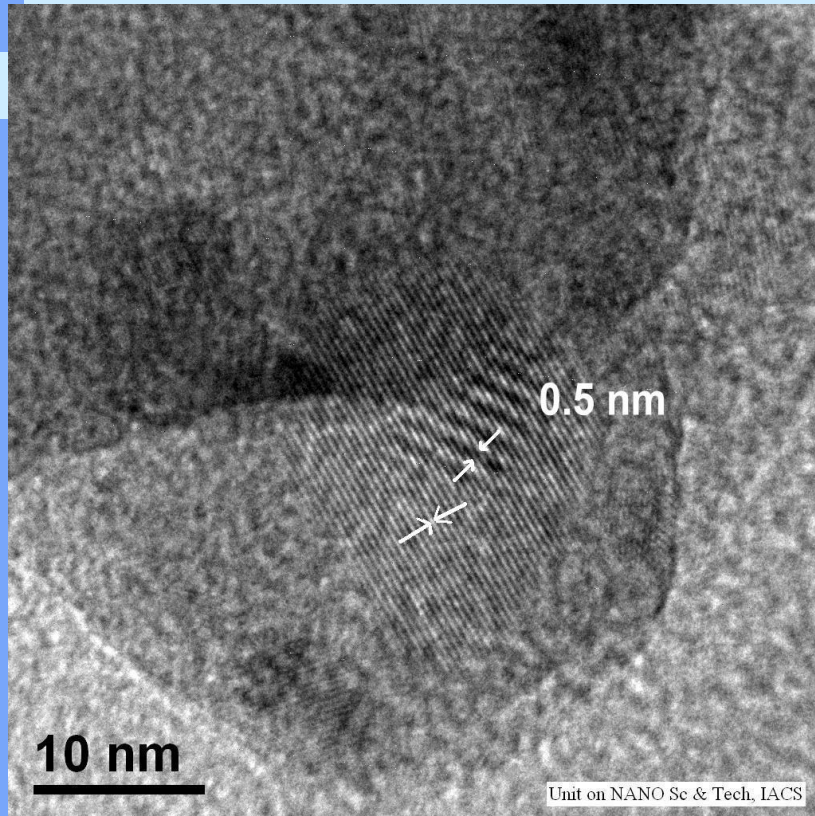


GLASS CERAMICS WITH FLUOROPHLOGOPITE MICA



SEM

NANOWIRES IN GLASS CERAMICS CONTAINING FLUOROPHLOGOPITE MICA

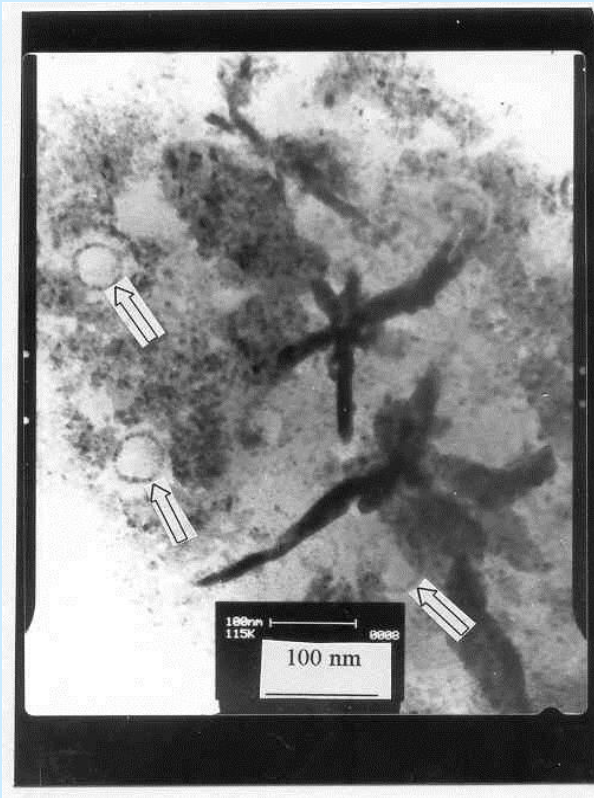


NANOWIRES IN GLASS CERAMICS CONTAINING FLUOROPHLOGOPITE MICA

Interplanar spacing d_{hkl} Specimen
heat treated at 1165 K / 2 hr +ion exchanged at 573 K / 24 hr

Experimental value Specimen heat treated at 1163K for 2 hr.and ion exchanged at 573 K for 24 hr. (nm)	Standard X-ray data for $K Mg_3Al Si_3$ $O_{10} F_2$ (nm)
1.0769	0.996 (001)
0.4666	0.459 (020)
0.375	0.365 (112)
0.304	0.313 (112)
0.250	0.249 (131)

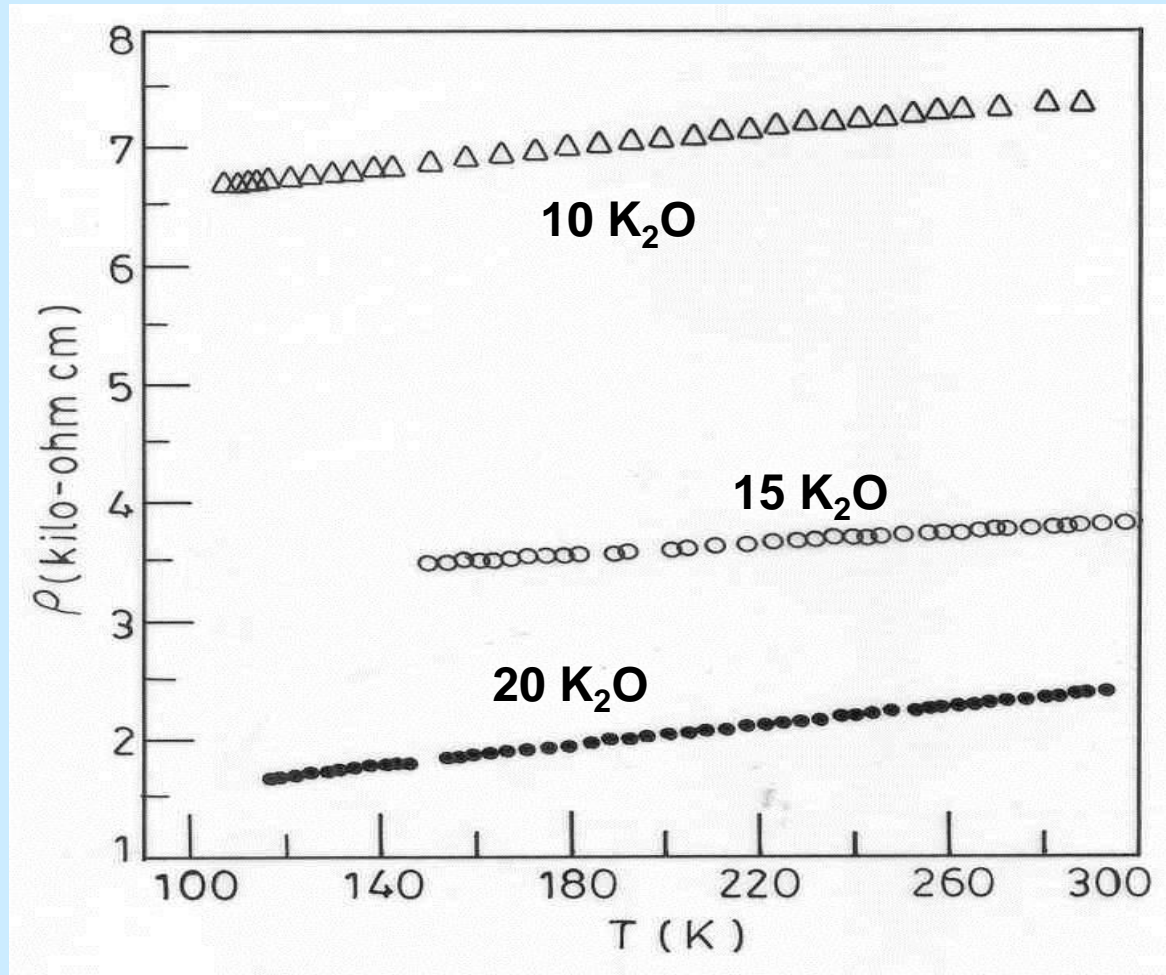
GROWTH OF SILVER NANO PARTICLES IN GLASS CERAMICS CONTAINING FLUORPHLOGOPITE MICA



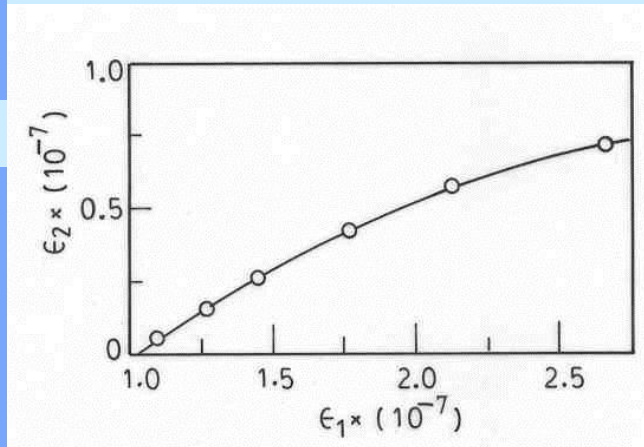
GLASS COMPOSITION

47 SiO₂ 15 B₂O₃ 12Al₂O₃ 10 MgO 10 K₂O 6KF

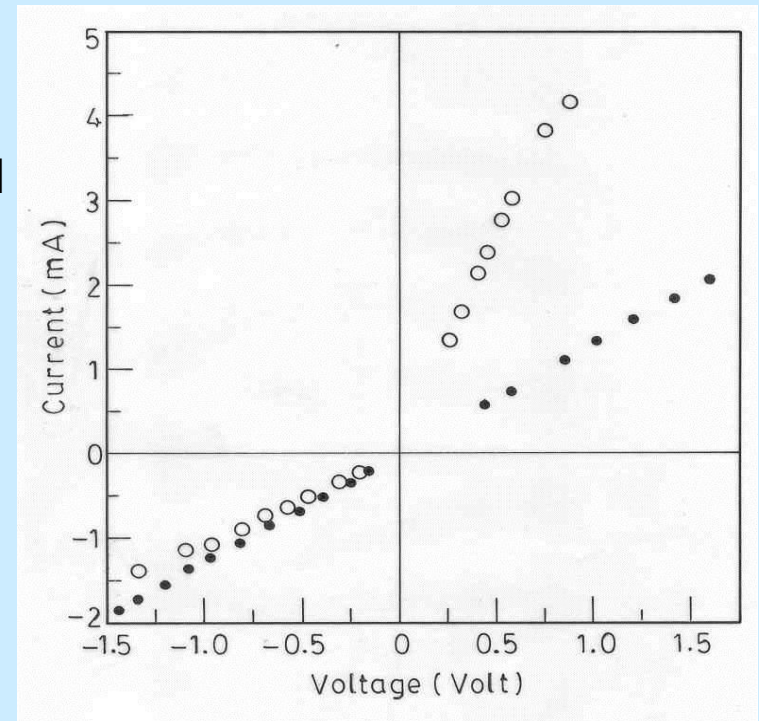
SILVER NANOWIRES IN GLASS CERAMICS CONTAINING FLUOROPHLOGOPITE MICA



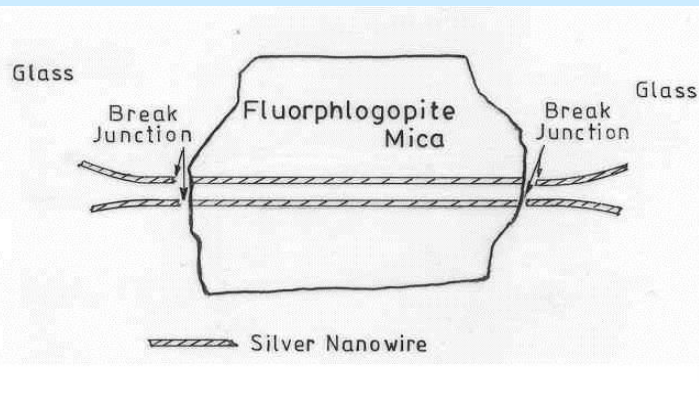
SILVER NANOWIRES IN GLASS CERAMICS CONTAINING FLUOROPHLOGOPITE MICA



COLE-COLE DIAGRAM



SCHEMATIC OF BREAK JUNCTIONS



SILVER NANOWIRES IN MICA CHANNELS– ULTRA HIGH DIELECTRIC PERMITTIVITY

***SPACE CHARGE POLARIZATION MODEL FAILS TO EXPLAIN HIGH ϵ
MECHANISM IS ELECTRONIC***

INTERRUPTED STRAND MODEL (RICE & BERNASCONI, 1972, PRL)

$$\epsilon \cong 1 / 2(q_s l_0)^2$$

l_0 : STRAND LENGTH ; $l_0 = 1287$ nm

q_s : FERMI THOMAS SCREENING WAVE VECTOR OF CONDUCTION ELECTRONS

$q_s \sim a^{-1}$ FOR METALLIC DENSITIES; FOR $\epsilon \sim 10^7$ AND $a = 0.28$ nm

IN AGREEMENT WITH MICA CRYSTALLITE DIMENSIONS

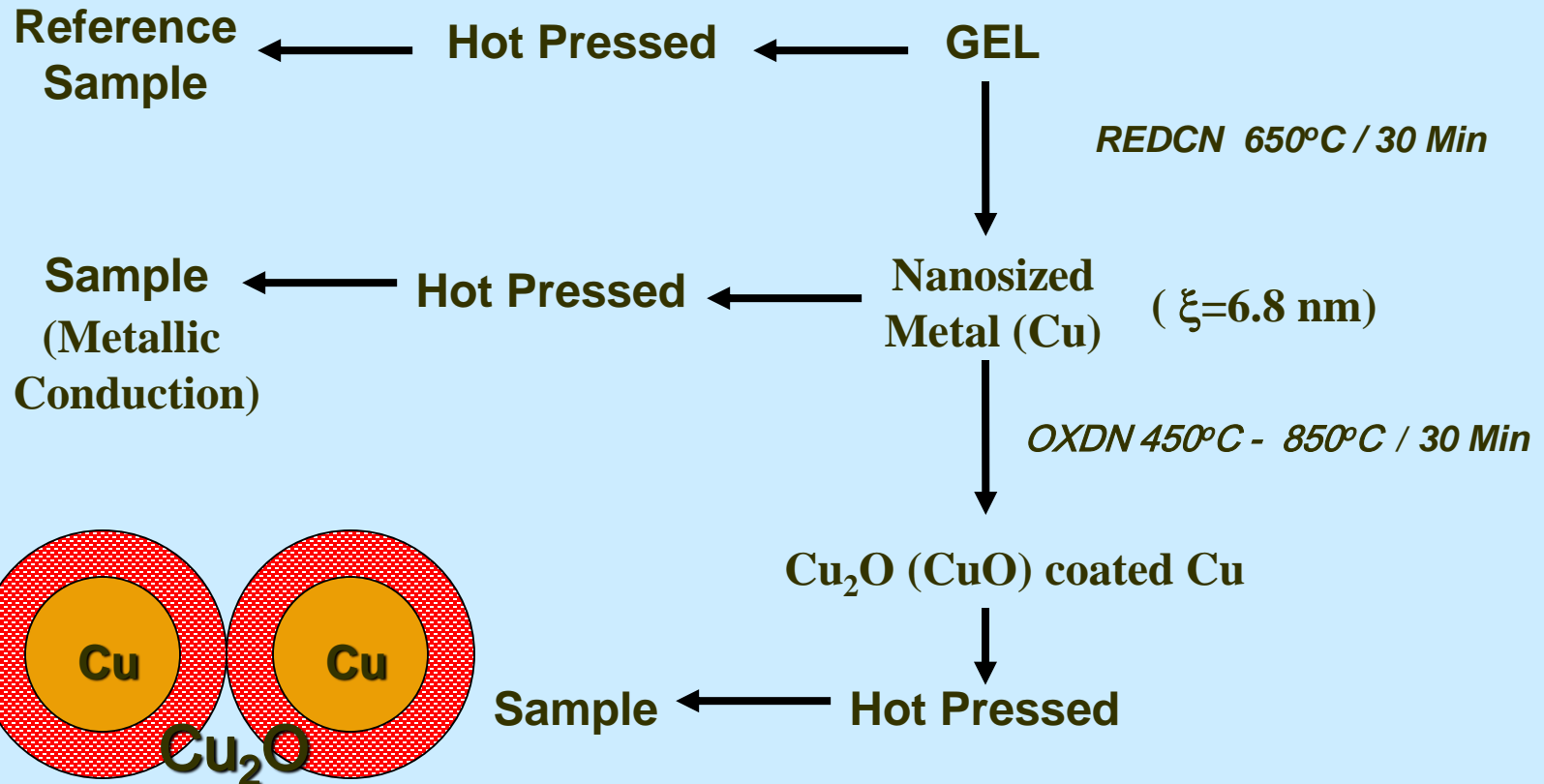
COPPER CORE COPPER OXIDE SHELL – INTERFACIAL AMORPHOUS PHASE

Preparation :

Target gel composition 60 CuO. 40 SiO₂ (mole%)

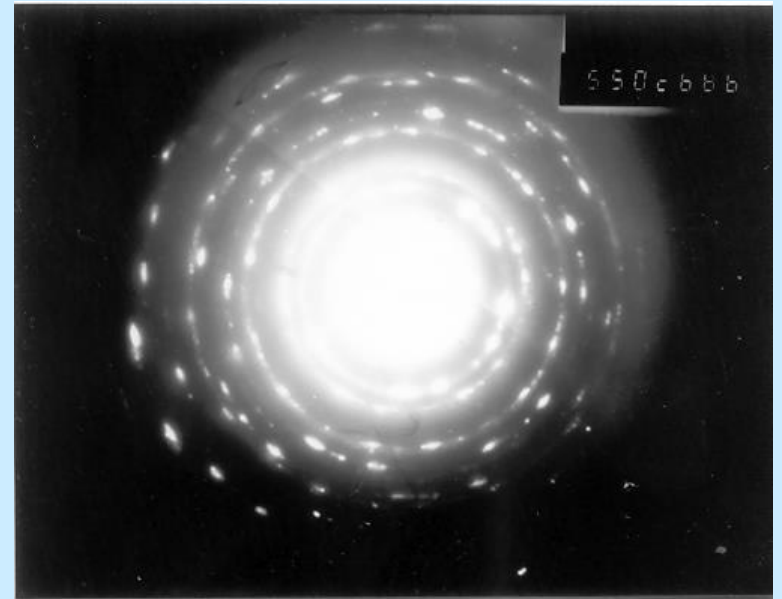
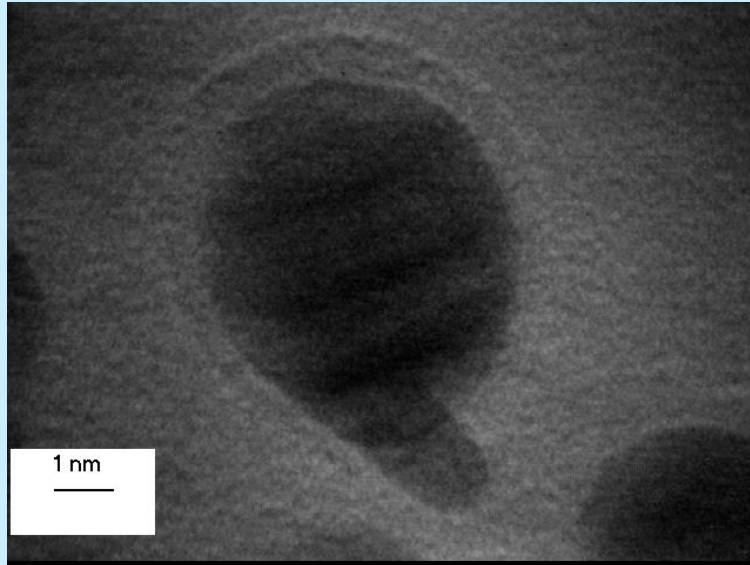
Precursors : CuCl₂ · 2H₂O, Si(OC₂H₅)₄

Solⁿ : 60 ml C₂H₅OH, 10 ml dist H₂O, 1 ml HCL, 125 ml Si (OC₂H₅)₄

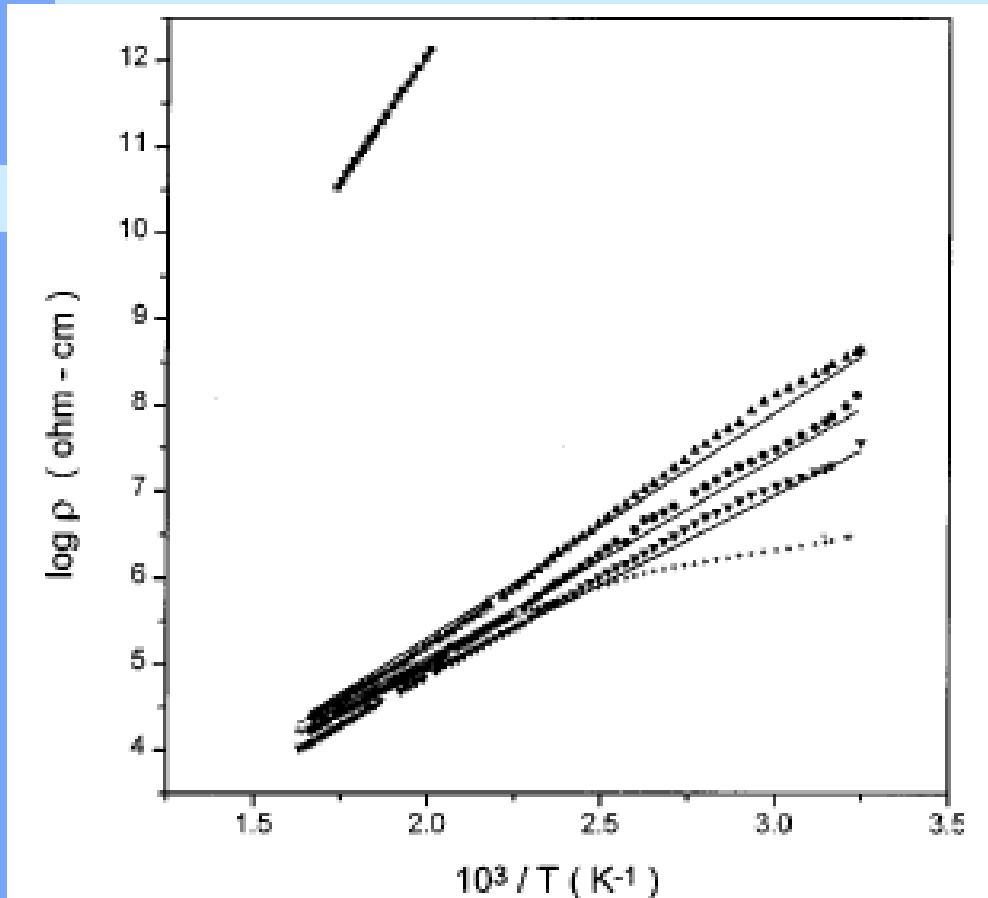


COPPER CORE COPPER OXIDE SHELL – INTERFACIAL AMORPHOUS PHASE

SPECIMEN REDUCED AT 923K / 30MIN + OXIDIZED AT 823K / 30MIN



COPPER CORE COPPER OXIDE SHELL-INTERFACIAL AMORPHOUS PHASE



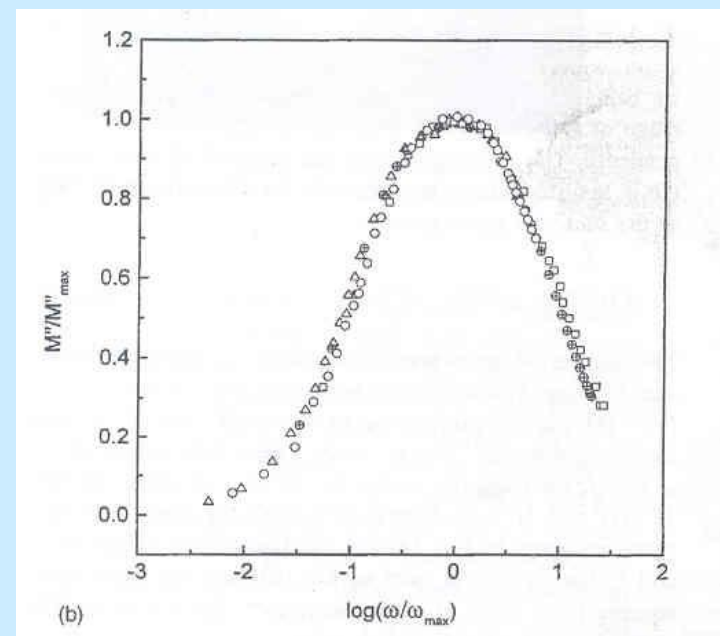
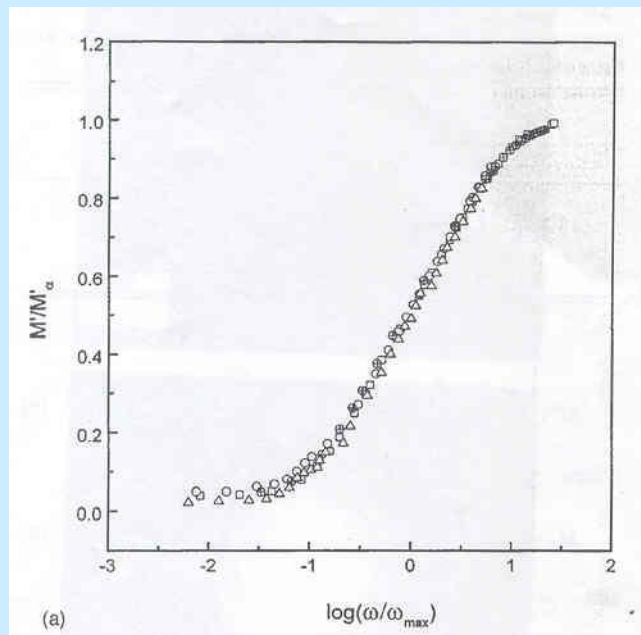
Variation of log resistivity as
a function of inverse
temperature for different samples.

Das/Chakravorty Appl.Phys.Lett. 76 ,1273 (2000)

COPPER CORE COPPER OXIDE SHELL – INTERFACIAL AMORPHOUS PHASE

NORMALIZED PLOTS OF M' AND M''
SPECIMEN REDUCED AT 923K / 30 MIN + OXIDIZED
AT 723K / 30 MIN

KWW FUNCTION : $F(t) = \exp[-(t/\tau_R)^\beta]$



COPPER CORE COPPER OXIDE SHELL – INTERFACIAL AMORPHOUS PHASE

Model	N/Wt	β_1	$10^{-5} \rho_0$	$10^k \tau_0$ (s)	$\varepsilon_{D\omega}$	$\varepsilon_{C1\omega}$	$10^5 A_{3C}$	γ_{3C}	$100S_P$	-FQF
CK1	12/P	{0.191}	3.42	[0.013]	72.5	0.754	2.98	89
CK1	12/M	{0.190}	3.33	[0.009]	74.1	0.602	2.34	124
CK1	10/P	[0.450]	3.05	[17.3]	{56.8}	16.3	1.87	96
CK1	10/M	{0.371}	3.04	[5.50]	{64.7}	8.49	1.52	119
CK1	10/P	(2/3)	3.06	135	{11.4}	66.0	2.60	83
CK1	10/M	(2/3)	3.02	118	{19.7}	58.7	1.93	114
CK1S	10/M	(2/3)	2.49	[59.5]	56.0	35.9	{1.17}	0.66	0.84	141
CK1S	10/M	0.676	2.55	68.3#	51.3#	39.6	(1.81)	0.64	0.90	138
CK1	10/P	(1/3)	3.10	2.94	65.8	6.43	1.97	94
CK1	10/M	(1/3)	3.06	2.67	67.4	5.90	1.53	120
CK1S	10/M	(1/3)	2.58	{1.40}	82.0	3.96	{1.53}	0.65	0.90	137
CK1S	10/M	0.438	2.57	8.56	76.4	9.92	(1.53)	0.66	0.77	143
CK1S	12/P	0.333	2.82	2.14	73.9	5.14	[1.42]	0.70	2.03	106
CK1S	12/P/Y	{0.331}	2.97	[2.46]	{69.8}	5.90	[1.58]	{0.73}	2.03	106

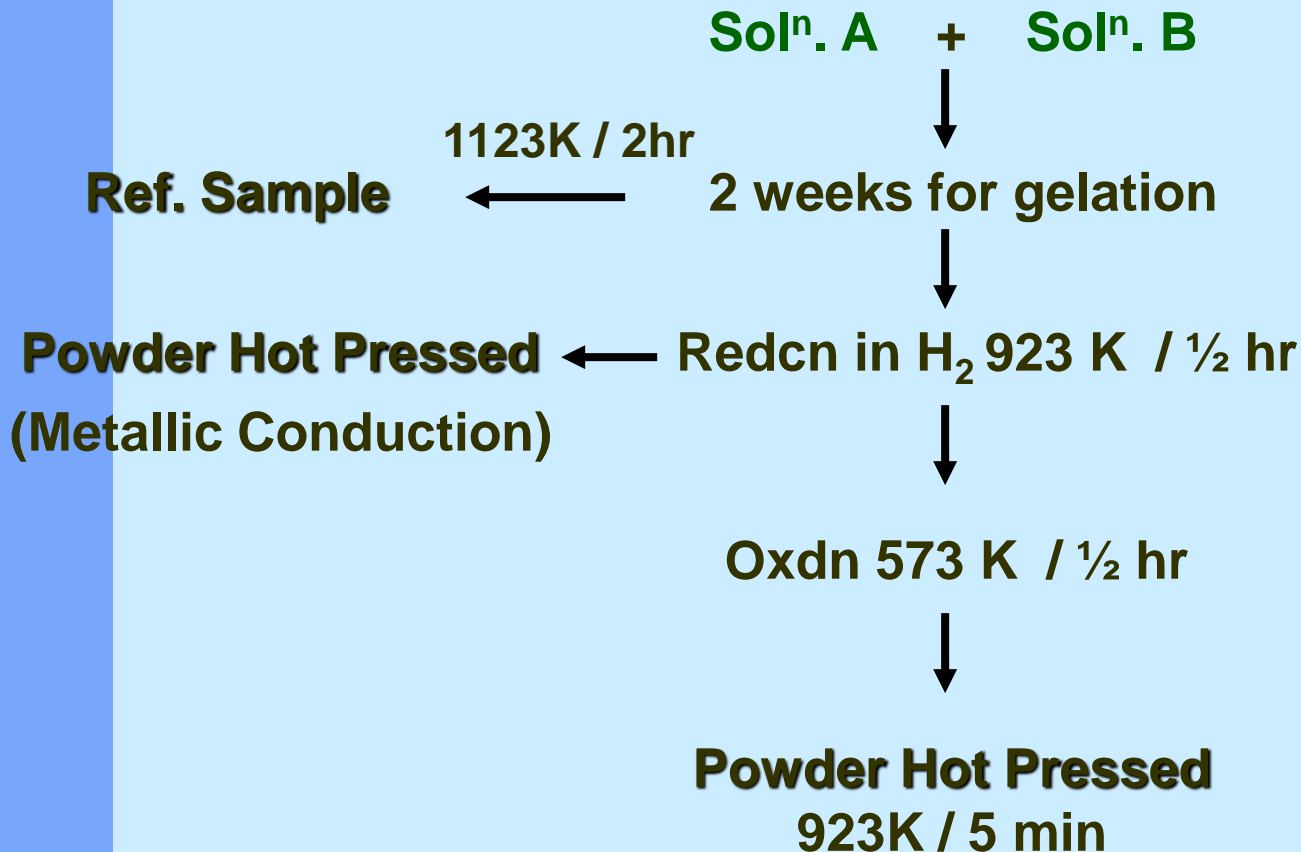
Macdonald Basu Chakravorty, J.Chem. Phys. 122, 241703,(2005)

Fe - Fe₃O₄ - SiO₂ Gel Nanocomposites

Target Composition :55 Fe₂O₃. 45 SiO₂ (mol %)

Solⁿ A :60 ml C₂H₅OH, 10ml H₂O, 23.17 gm FeCl₃

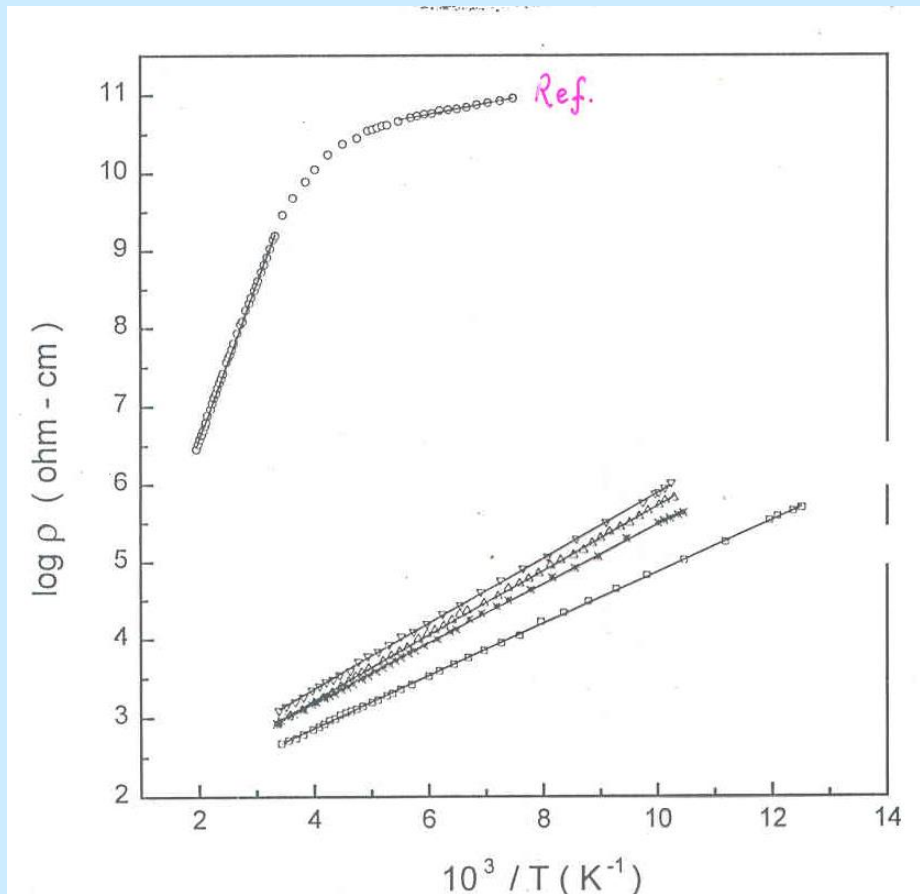
Solⁿ B :90 ml C₂H₅OH, 15ml H₂O, 1 ml HCL
26.2 ml Si(OC₂H₅)₄



Fe - Fe₃O₄ - SiO₂ Gel Nanocomposites

Heat treatment Schedule for gel powder before hot pressing	Median Diameter X (nm)	Geometric Standard Deviation σ
Reduced at 923 K / ½ hr	5.3	1.4
Reduced at 923 K / ½ hr Oxidized at 823 K / ½ hr X	4.9	1.4
Reduced at 923 K / ½ hr Oxidized at 1023 K / ½ hr	4.6	1.4
Reduced at 923 K / ½ hr Oxidized at 1123 K / ½ hr	4.4	1.4
Reduced at 923 K / ½ hr Oxidized at 1123 K / ½ hr	4.2	1.4
Reduced at 923 K / ½ hr Oxidized at 1123 K / ½ hr	4.1	1.4

Fe-Fe₃O₄/SiO₂ Nanocomposites



- ▽ 4.9 nm
- △ 4.6 nm
- ★ 4.4 nm
- ◻ 4.2 nm

Das et al J.Appl.Phys. 914573 (2002)

Fe - Fe₃O₄ - SiO₂ Gel Nanocomposites

specimen	W (eV)	α (Å ⁻¹)	R (Å)	C	ν_0 (s ⁻¹)	ϵ_p
Ref	0.39	0.95	4.7	0.99	1.2x10 ¹³	4.9
2	0.08	0.89	4.7	0.99	1.3x10 ¹³	23.8
3	0.08	0.86	4.8	0.99	1.2x10 ¹³	23.3
4	0.07	0.87	4.9	0.99	1.1x10 ¹³	26.1
5	0.06	0.86	4.8	0.99	1.3x10 ¹³	31.1

Small polaron Hopping

$$\rho = \frac{kTR}{\nu_0 c^2 c(1-c)} \exp(2\alpha R) \exp\left(\frac{W}{kT}\right)$$

$$W \approx e^2 / 4\epsilon_p \gamma_p$$

$$\gamma_p = \frac{1}{2} \left(\frac{\Pi}{6}\right)^{1/3} R$$

SILVER / SILICATE GLASS CERAMIC NANOCOMPOSITES

COMPOSITION :

10 Na₂O, 34 BaO, 34 TiO₂, 17 B₂O₃, 5 SiO₂



Heat treatment at 843 K and 963 K



Powdered samples ION Exchanged at 583 K / 6 Hrs



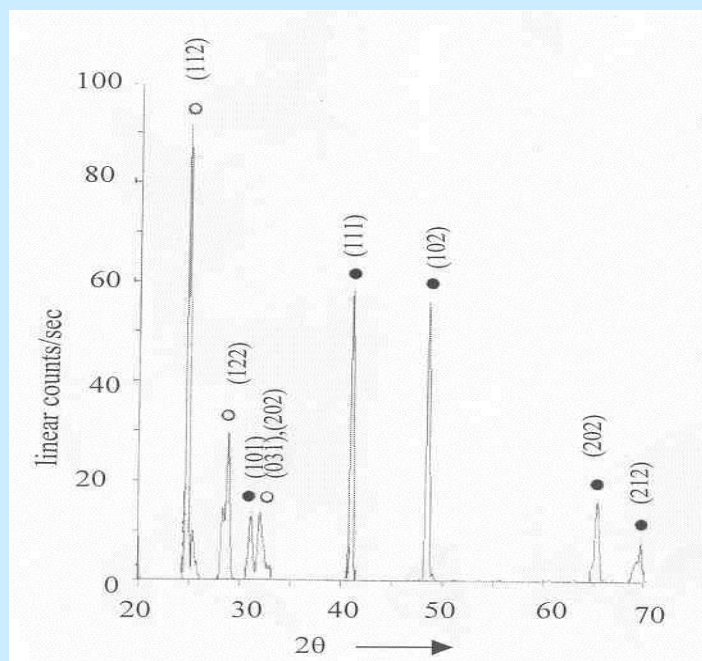
Reduction at 573 K / 5 Min.s

SILVER / SILICATE GLASS CERAMIC NANOCOMPOSITES

SEM Micrograph
of Glass Ceramic

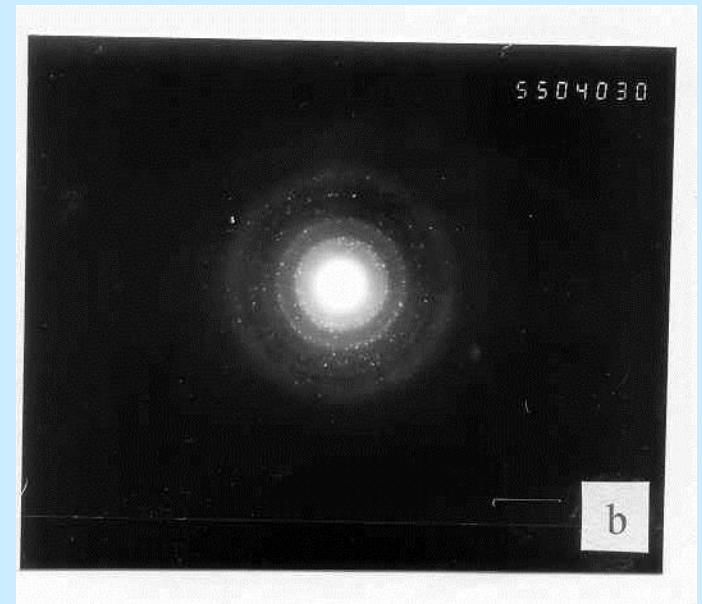
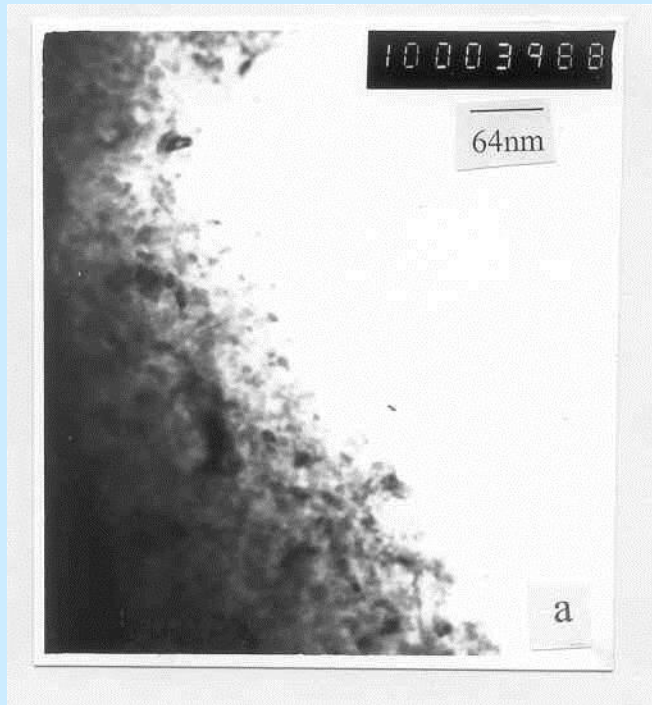


X Ray Diffractogram
of Glass Ceramic



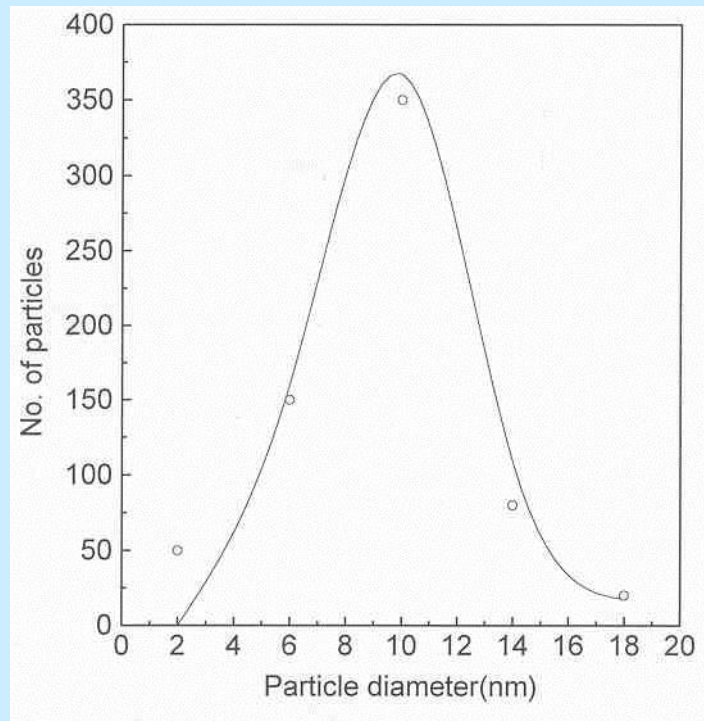
Crystalline phases : $\text{Na}_2\text{B}_4\text{O}_7$; BaTiO_3

SILVER / SILICATE GLASS CERAMIC NANOCOMPOSITES



- a) TEM of ION Exchanged and reduced Glass Ceramic
- b) Electron Diffraction of (a)

SILVER / SILICATE GLASS CERAMIC NANOCOMPOSITES



Histogram of Silver Particle Size

SILVER / SILICATE GLASS CERAMIC NANOCOMPOSITES

Table II

Summary of heat treatment schedules for crystallization and median diameter \bar{x} and geometric standard deviation σ obtained for different specimens after ion exchange/reduction treatment

Specimen No.	Heat Treatment Schedule	\bar{x} (nm)	σ
1	843K for 2 hours + 963K for 10 min.	3.4	1.5
2	843K for 4 hours + 963K for 10 min.	4.6	1.3
3	843K for 6 hours + 963K for 15 min.	10.1	1.3
4	843K for 2 hours + 963K for 20 min.	13.2	1.4

Reduction in Hydrogen at 573 K / 5 Min.s

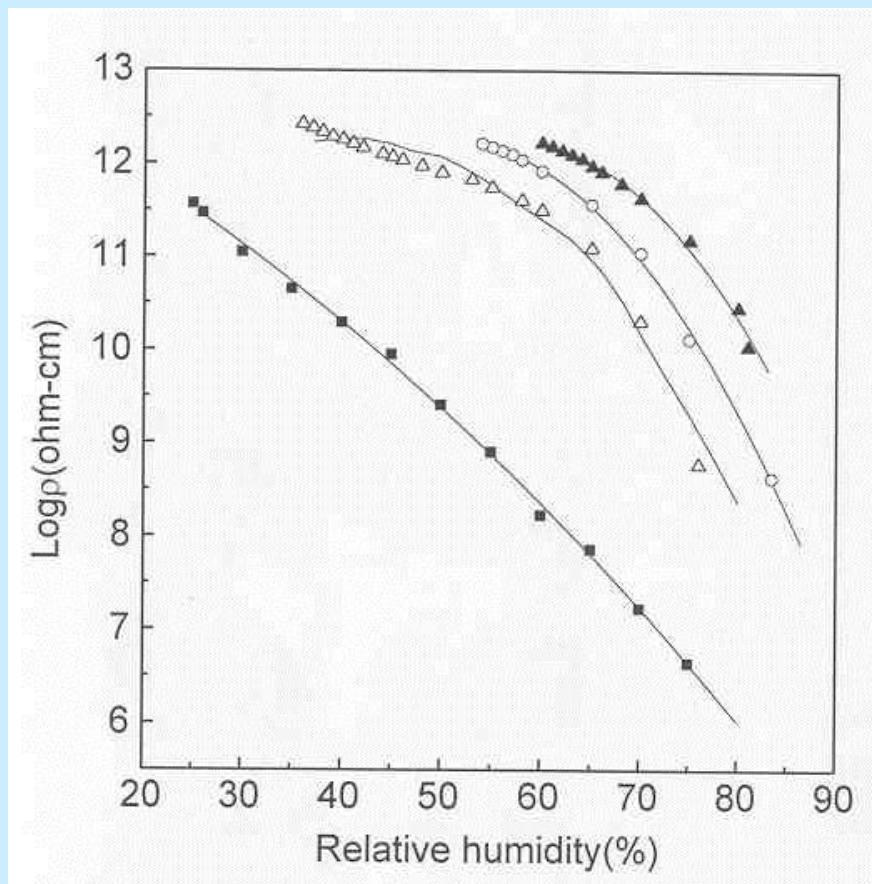
SILVER / SILICATE GLASS CERAMIC NANOCOMPOSITES

▲ 3.4 nm

○ 4.6 nm

■ 10.1 nm

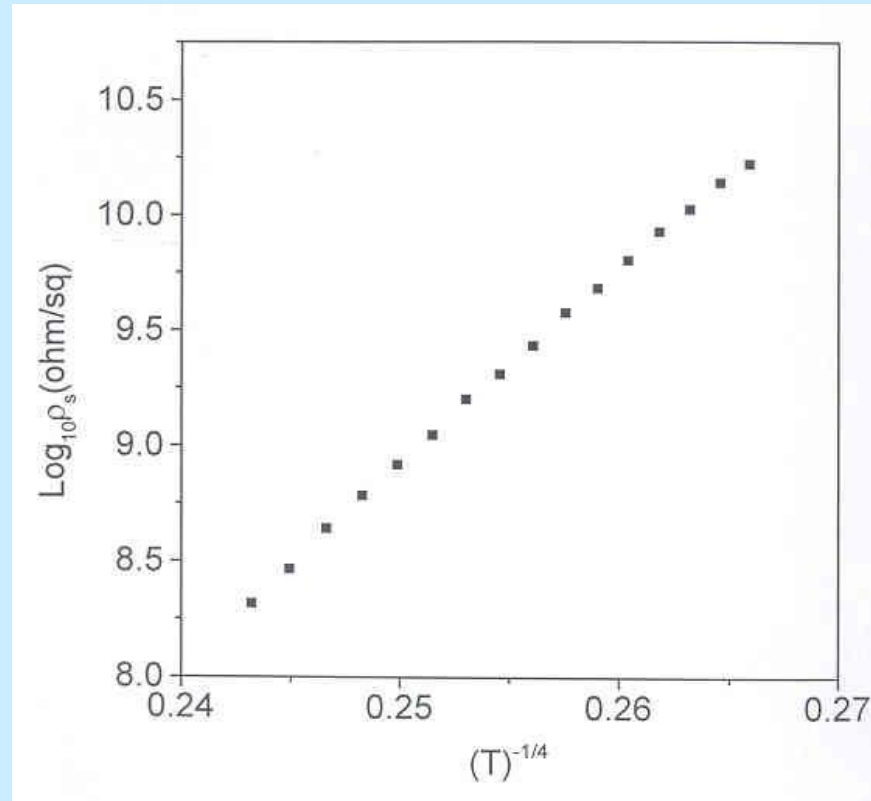
△ 13.2 nm



Resistivity vs. Relative Humidity

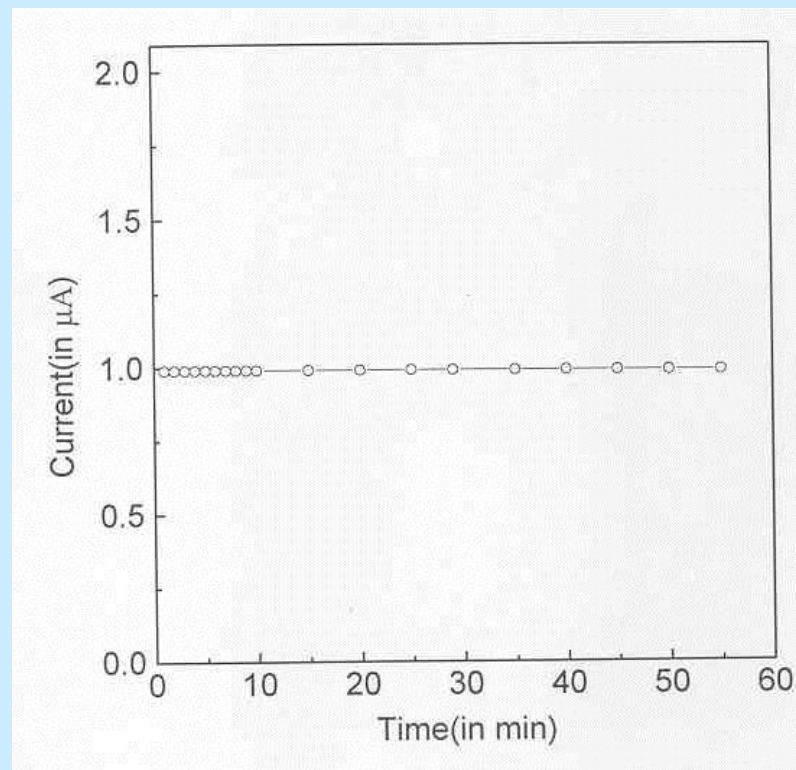
Pal et al J.Appl.Phys. 93, 4201 (2003)

SILVER / SILICATE GLASS CERAMIC NANOCOMPOSITES



Surface Resistivity vs. $T^{-1/4}$
Particle Diameter 3.4 nm

SILVER / SILICATE GLASS CERAMIC NANOCOMPOSITES



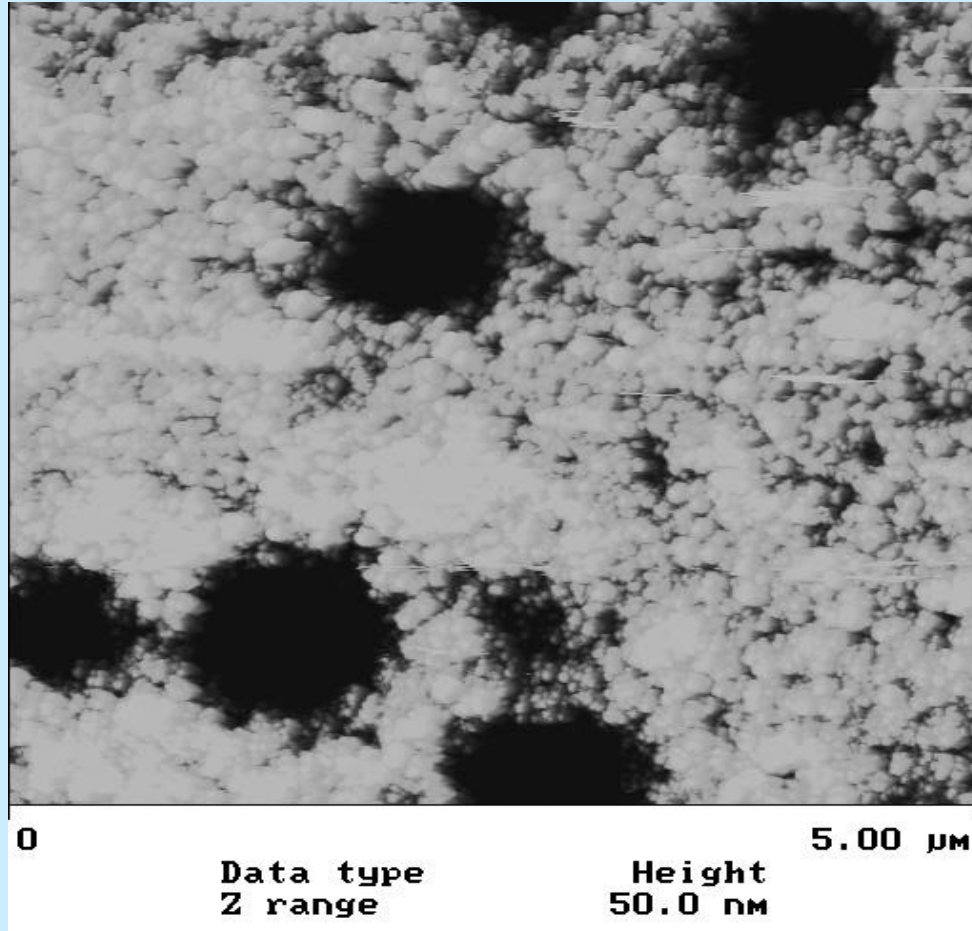
Current vs. Time
Silver Particle Diameter 10.1 nm
Relative Humidity 85 %

IRON-IRON OXIDE NANO CORE-SHELL STRUCTURE



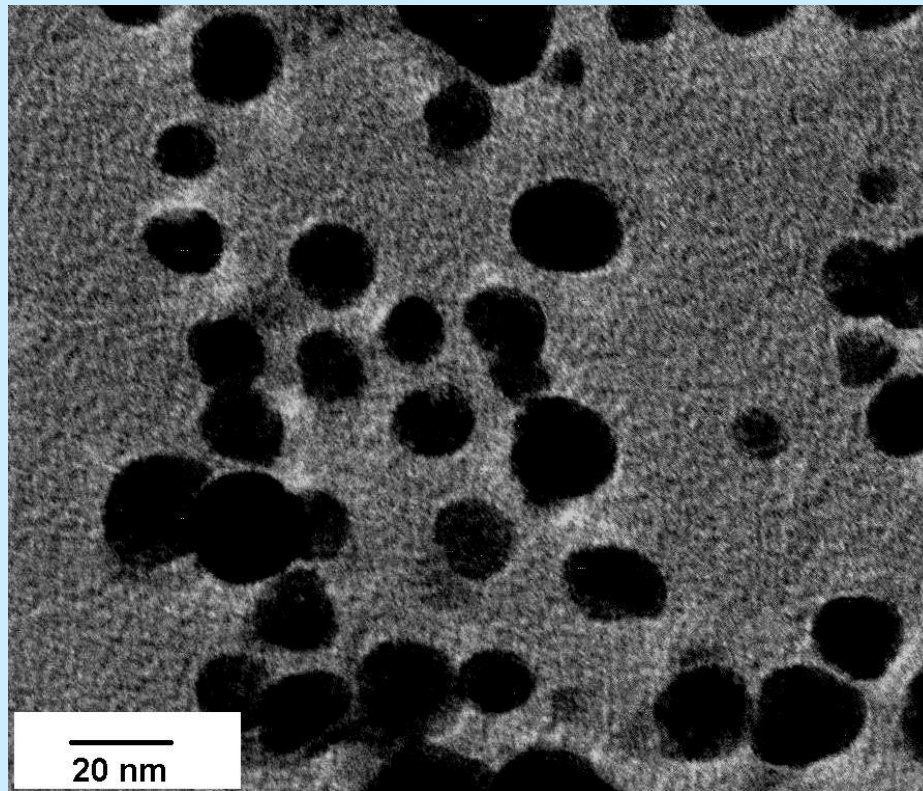
Optical micrograph of film with fractally grown Fe-
Fe₃O₄ core shell structure

IRON-IRON OXIDE NANO CORE-SHELL STRUCTURE



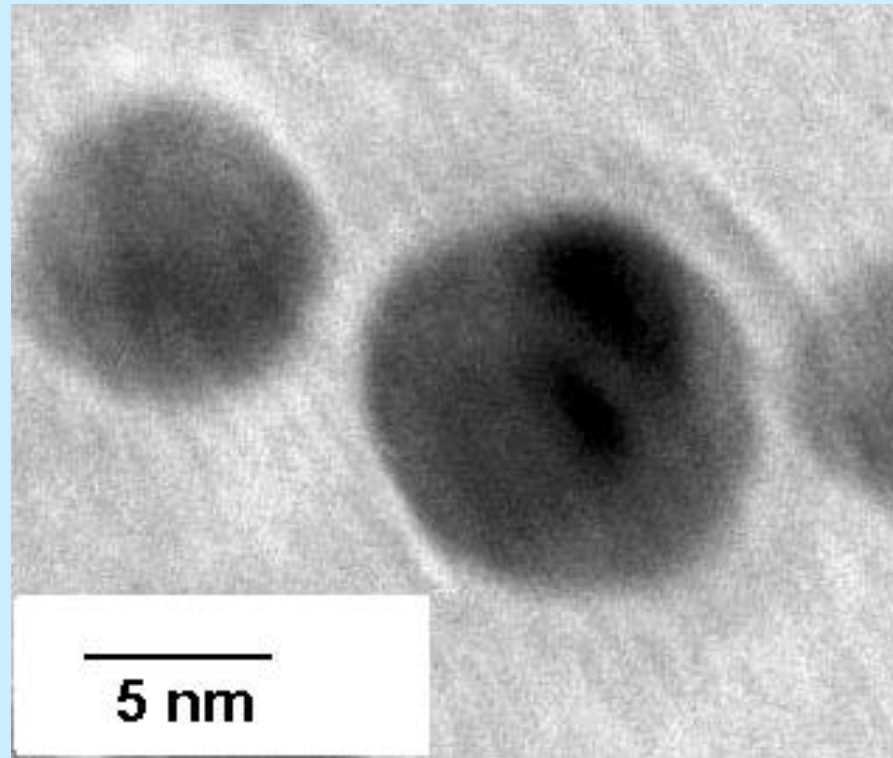
AFM micrograph

IRON-IRON OXIDE NANO CORE-SHELL STRUCTURE



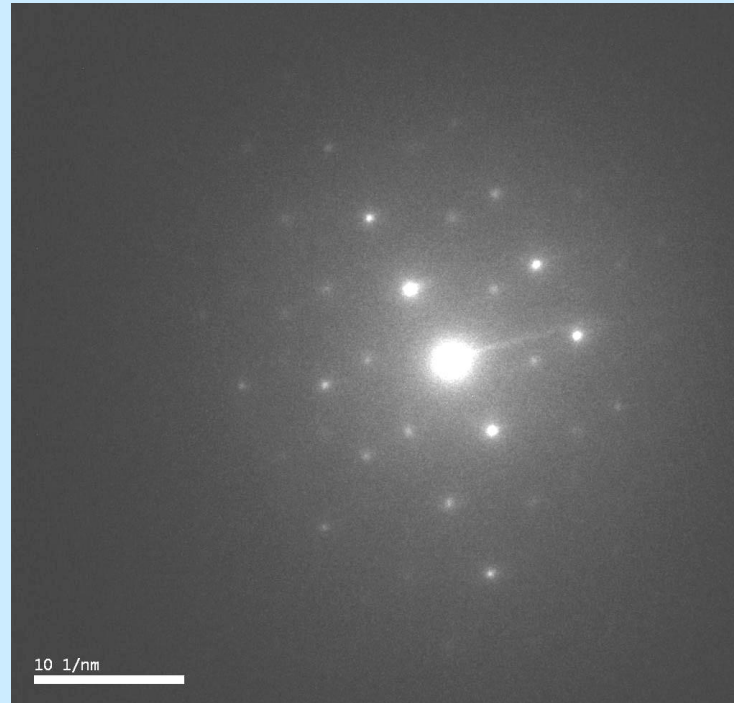
TEM of the specimen

IRON-IRON OXIDE NANO CORE-SHELL STRUCTURE



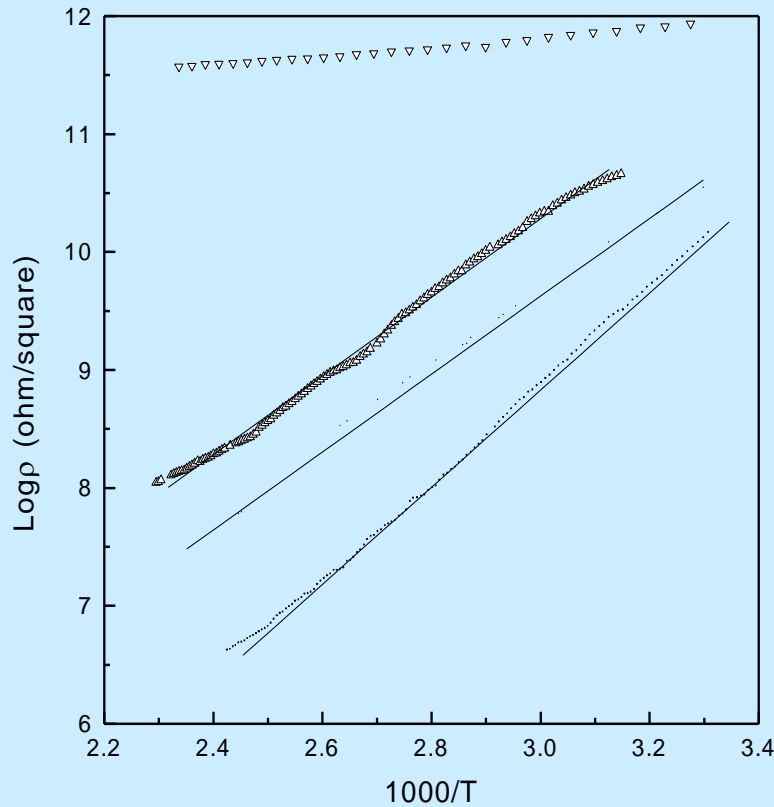
TEM of core shell structure

IRON-IRON OXIDE NANO CORE-SHELL STRUCTURE



Electron diffraction pattern IRON-IRON OXIDE
NANO CORE-SHELL STRUCTURE

IRON-IRON OXIDE NANO CORE-SHELL STRUCTURE



Surface resistivity as a function of temperature

▽ Reference

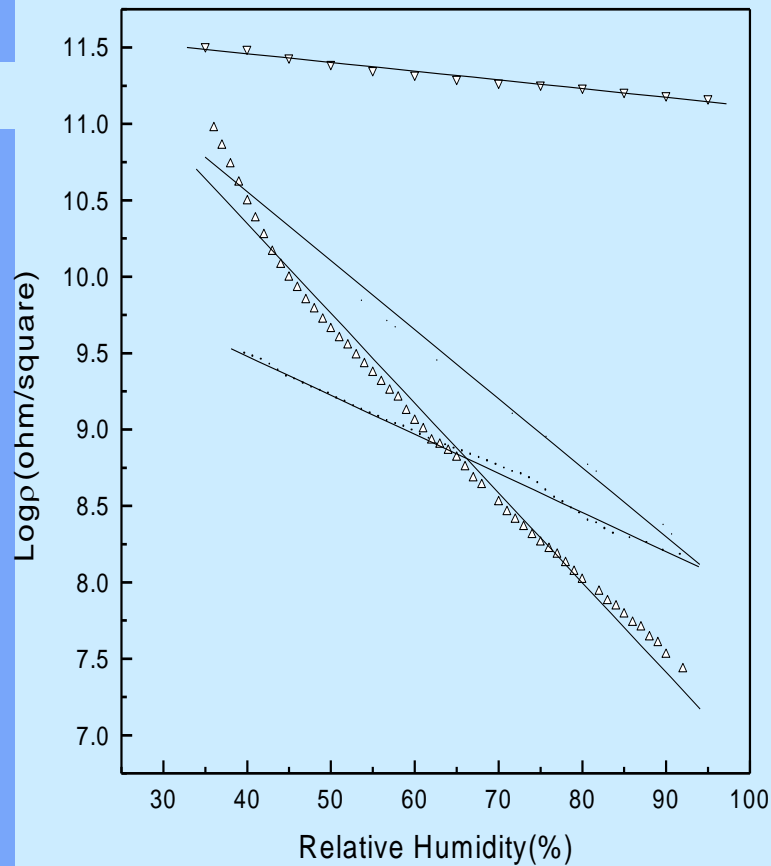
Specimen

○ 1 hour oxidation

□ 2 hour oxidation

△ 4 hour oxidation

IRON-IRON OXIDE NANO CORE-SHELL STRUCTURE



Surface resistivity vs. relative humidity

- ▽ Reference Specimen
- 1 hour oxidation
- 2 hour oxidation
- △ 4 hour oxidation

Pal et.al. J.Appl.Phys.97,034311(2005)

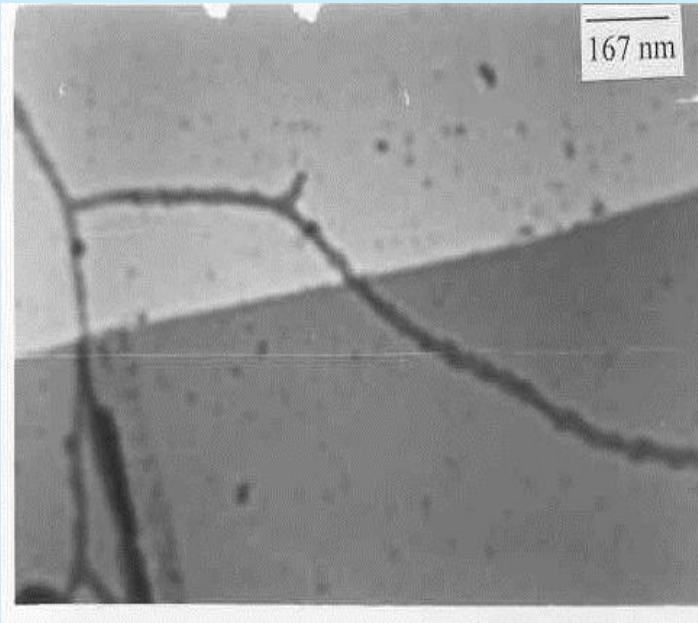
NANO INTERFACES IN GLASS METAL NANOCOMPOSITES

GLASS COMPOSITION : 30 Li₂O 12 CaO 3 Al₂O₃ 55 SiO₂

ION EXCHANGED IN AgNO₃ AT 573 K FOR 11 HRS

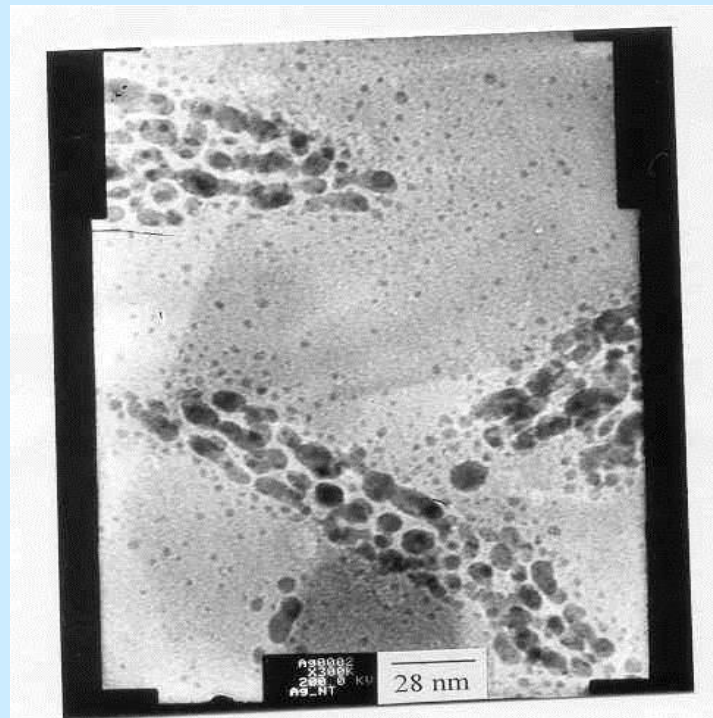
**ELECTRODEPOSITION AT 600 K, 5 and 10 VOLTS
FOR 10 HRS**

NANO INTERFACES IN GLASS METAL NANOCOMPOSITES



**TEM
OF SILVER NANO ARRAYS**

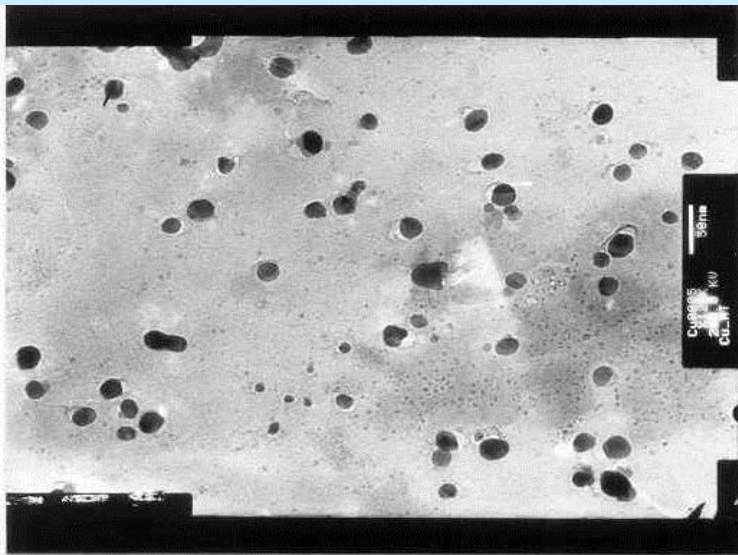
NANO INTERFACES IN GLASS METAL NANOCOMPOSITES



**TEM OF NANO ARRAYS
OF SILVER IN
SILICATE GLASS**

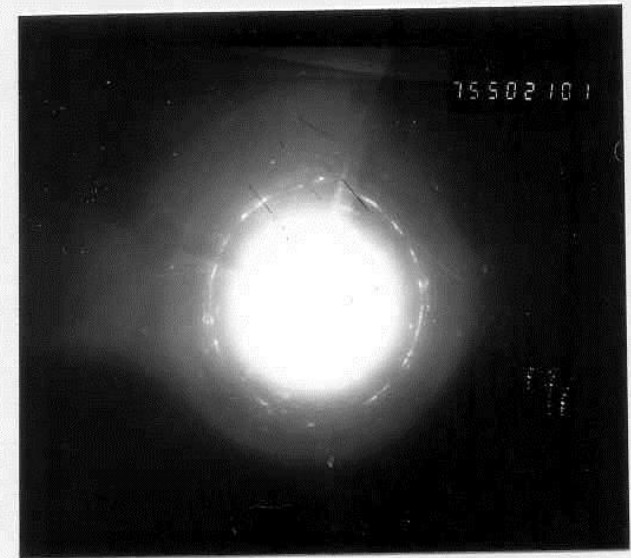
NANO INTERFACES IN GLASS METAL NANOCOMPOSITES

TEM OF SILICA GEL GLASS WITH COPPER NANO ARRAYS

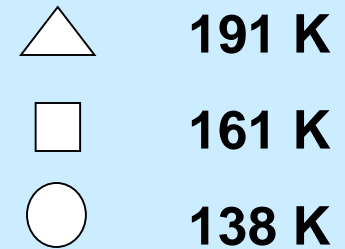
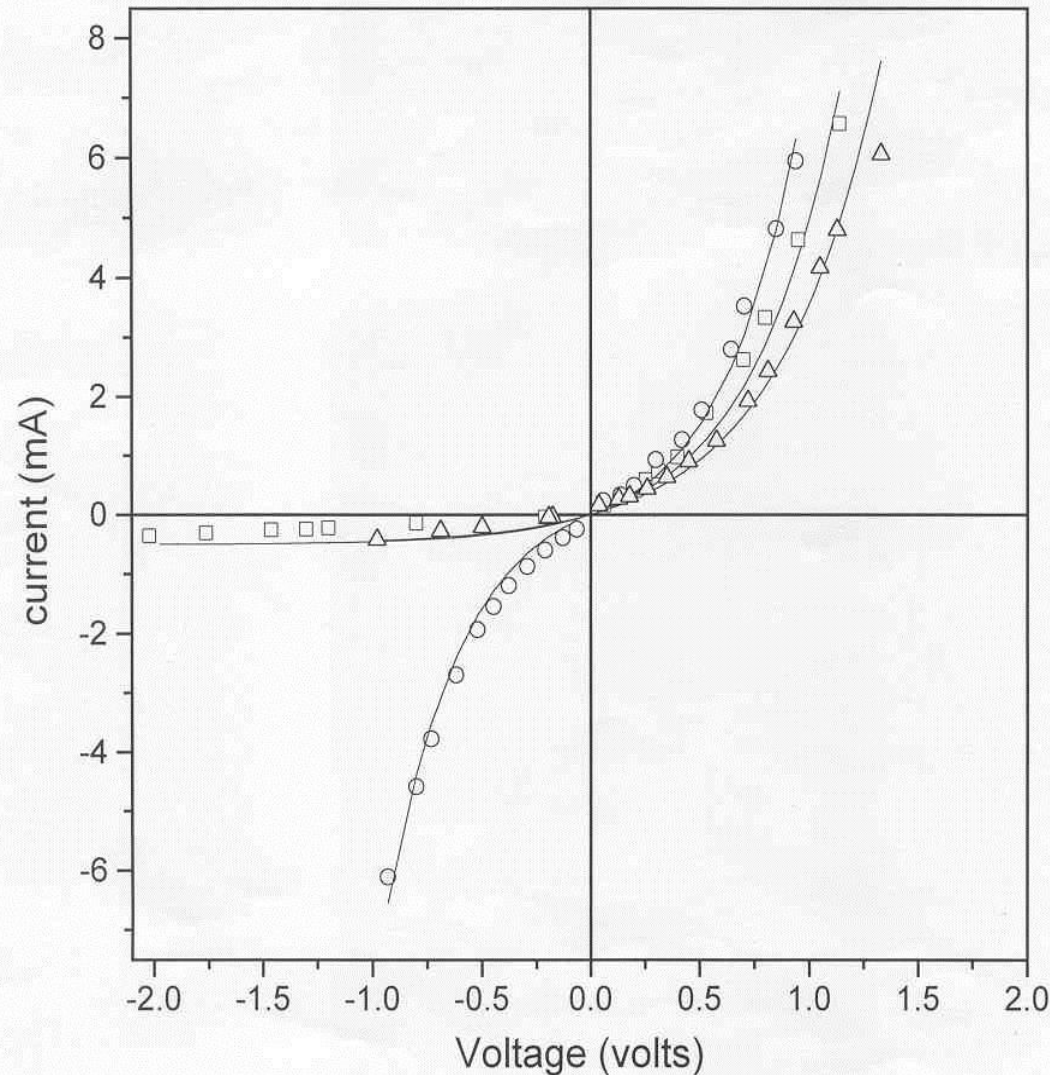


COMPOSITION : $30\text{Cu}(\text{NO}_3)_2$ 70SiO_2

ELEKTRODEPOSITION VOLTAGE : 5 VOLTS



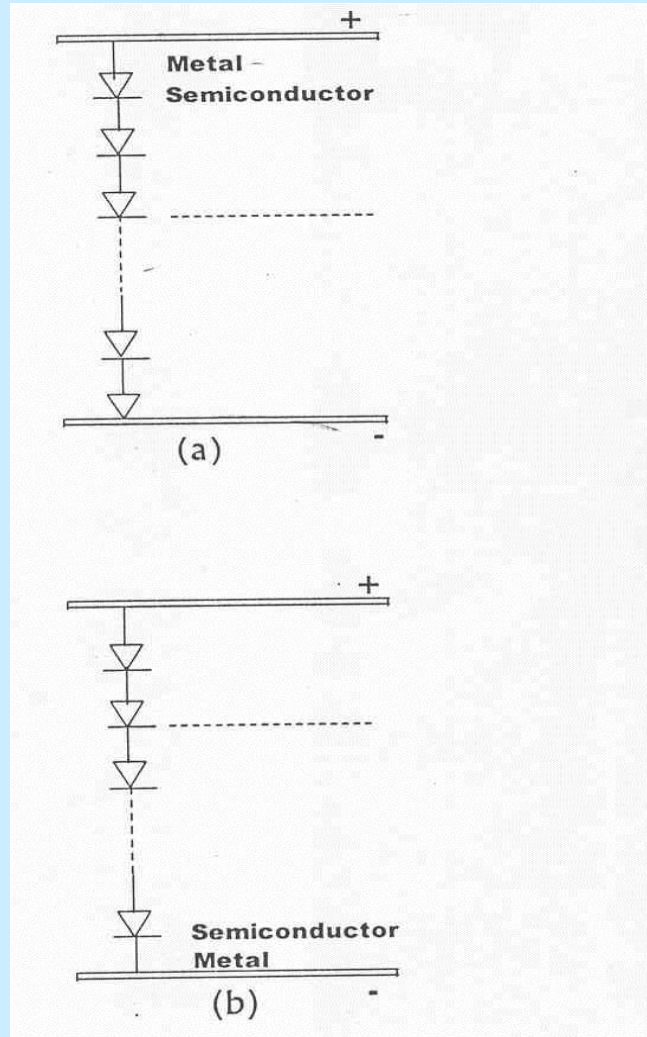
NANO INTERFACES IN GLASS METAL NANOCOMPOSITES



GLASS COMPOSITION
 $30\text{Li}_2\text{O}$ 12CaO $3\text{Al}_2\text{O}_3$ 55SiO_2

ELECTRO DEPOSITION
VOLTAGE : 5 VOLTS

NANO INTERFACES IN GLASS METAL NANOCOMPOSITES

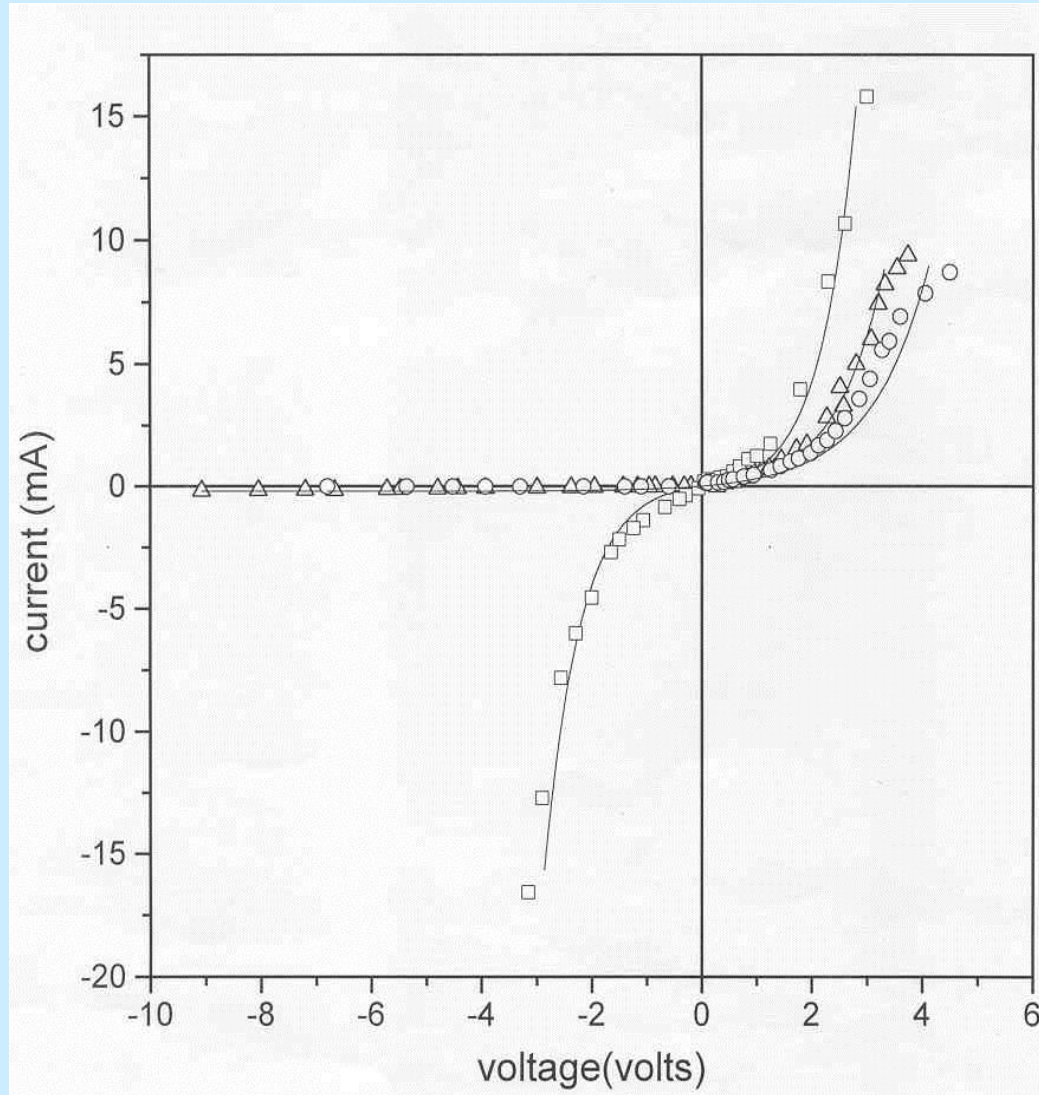


DIODE LIKE BEHAVIOUR

**SCHEMATIC REPRESENTATION OF
METAL SEMICONDUCTOR
NANO JUNCTION ARRAYS**

SYMMETRICAL NON LINEAR V - I

NANO INTERFACES IN GLASS METAL NANOCOMPOSITES

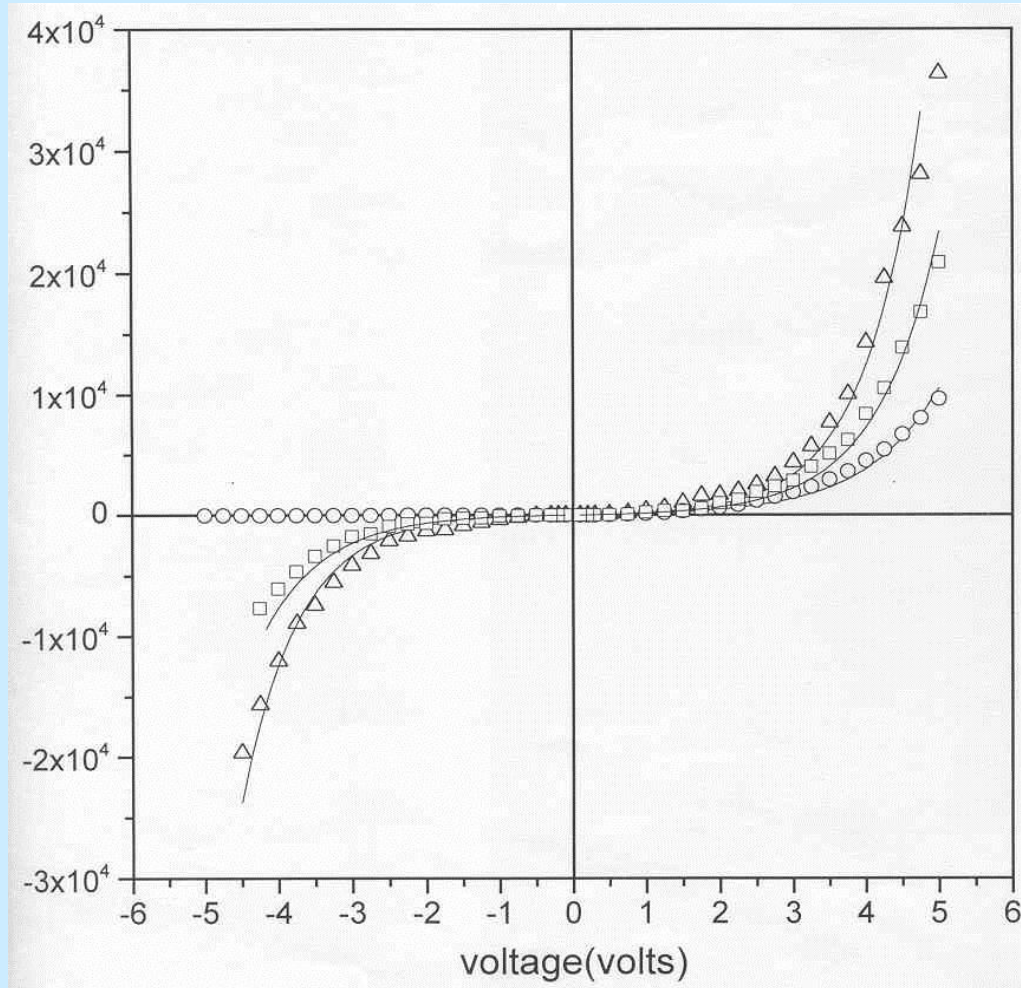


- △ 208 K
- 167 K
- 125 K

30 Li₂O 12CaO 3Al₂O₃ 55SiO₂

ELECTRODEPOSITION
AT 10 VOLTS

NANO INTERFACES IN GLASS METAL NANOCOMPOSITES



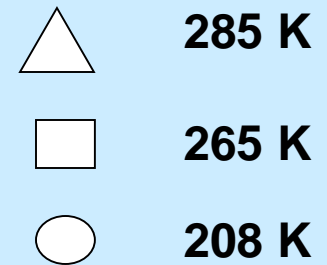
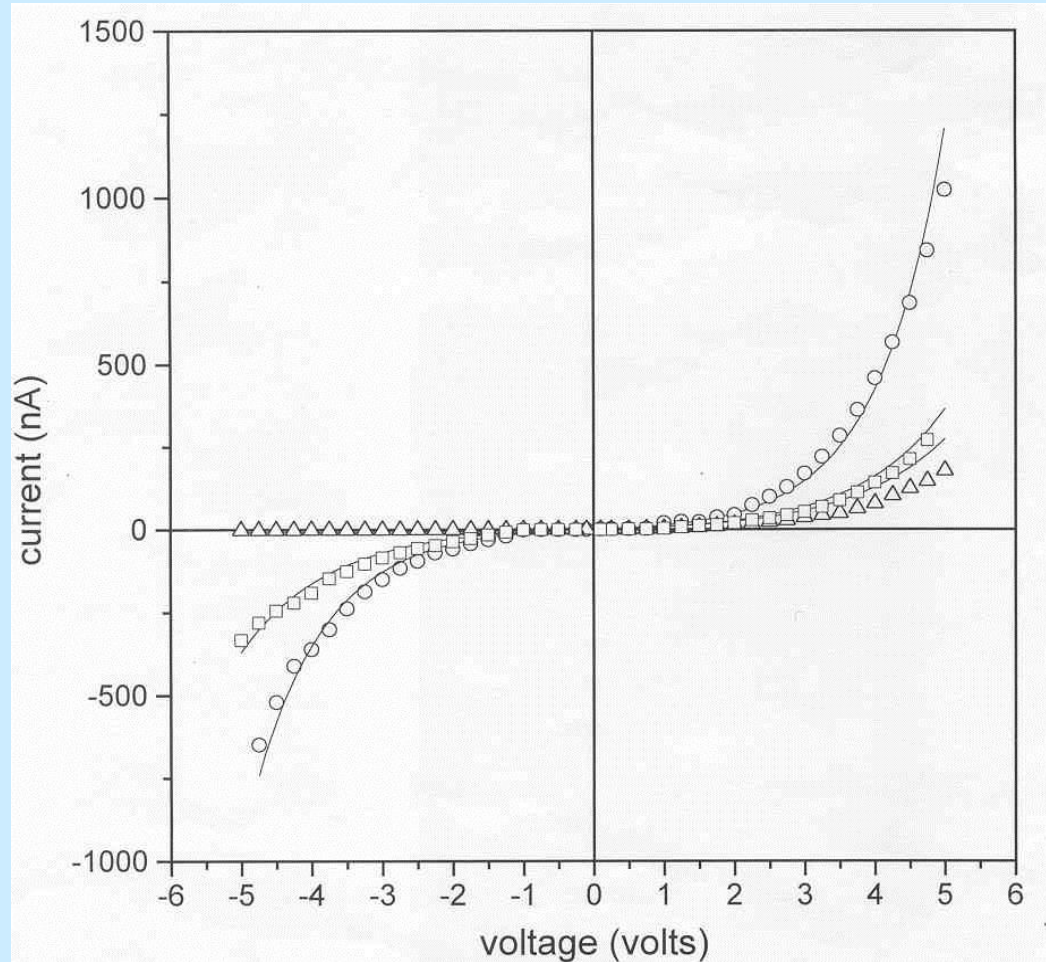
○ 275 K
□ 238 K
△ 213 K

30Cu(NO₃)₂ · 70SiO₂ GEL

ELEKTRODEPOSITION
AT 5 VOLTS

Dan et al J.Appl.Phys. 93,4794 (2003)

NANO INTERFACES IN GLASS METAL NANOCOMPOSITES



30Cu(NO₃)₂ · 70SiO₂ GEL

ELETRODEPOSITION
AT 10 VOLTS

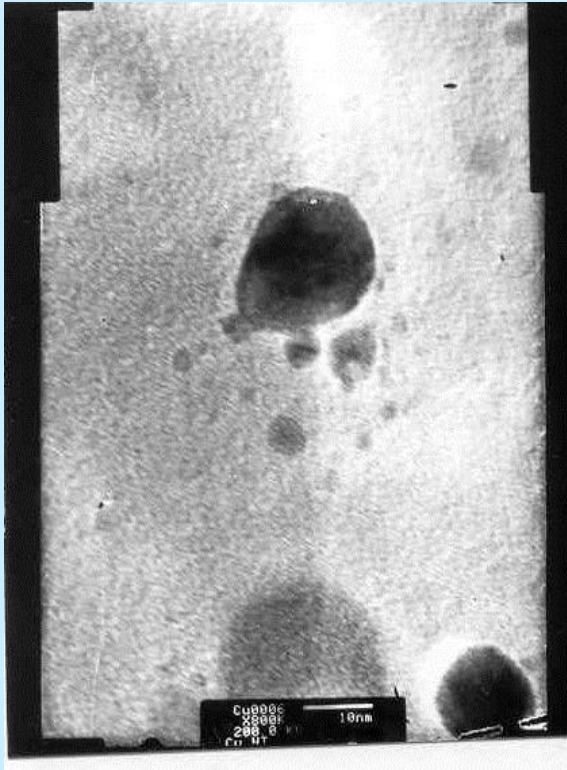
NANO INTERFACES IN GLASS METAL NANOCOMPOSITES

DATA FITTED TO

$$I = I_0 \left[\exp\left(\frac{eV}{nkT}\right) - 1 \right]$$

COMPOSITION	ELECTRO DEPOSITION VOLTAGE	I_0 (Amp)	n
1	5	0.5×10^{-3}	30
1	10	0.2×10^{-3}	60
2	5	0.7×10^{-7}	42
2	10	0.07×10^{-7}	55

NANO INTERFACES IN GLASS METAL NANOCOMPOSITES



ELECTRODEPOSITION
VOLTAGE 5 VOLTS

TEM OF A NANO INTERFACE
BETWEEN TWO COPPER PARTICLES

CONCLUSIONS

- Silicate glasses can be used as effective templates for nanostructure growth
- Glass nanocomposites show novel properties
- New functionalities can be generated by using a nanocomposite approach in glasses

THANK YOU