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from the 17th University Glass Conference

Université Montpellier II

Ion diffusion in chalcogenide glasses Application in ionics and optics

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Chalcogenide Glasses

Chalcogenide glasses are glasses containing chalcogens (Se, S, Te).

Chalcogenide homologous of oxide glasses

SiO_2 ; GeO_2 --> $SiS(e)_2$; $GeS(e)_2$

Ia																0
1 H	IIa											IIIa	IVa	Va	VIa	VIIa	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg	IIIb	IVb	Vb	VIb	VIIB	VIIIb			Ib	IIb	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Unq	105 Unp	106 Unh	107 Uns											
				58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
				90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Chalcogenide Glasses

Presence of S, Se, Te --> polarisable environment with lone-pair (LP)

↓

Specific property of chalcogenide glasses compared to oxide ones

They exhibit semiconductor properties and thus form a large group of amorphous semiconductors
Intrinsically metastable, they can undergo various structural transformations under the action of external stimuli, in particular light.

Semiconductor

As_2S_3 glass
$\sigma \sim 10^{-14}$ Scm^{-1}
Eg ~ 2,15 eV

Photoinduced phenomena

$h\nu$ -> hole-electron pair -> change in n

Ovshinsky effect
(amorphous state <-> crystalline state)

Transparency in the IR

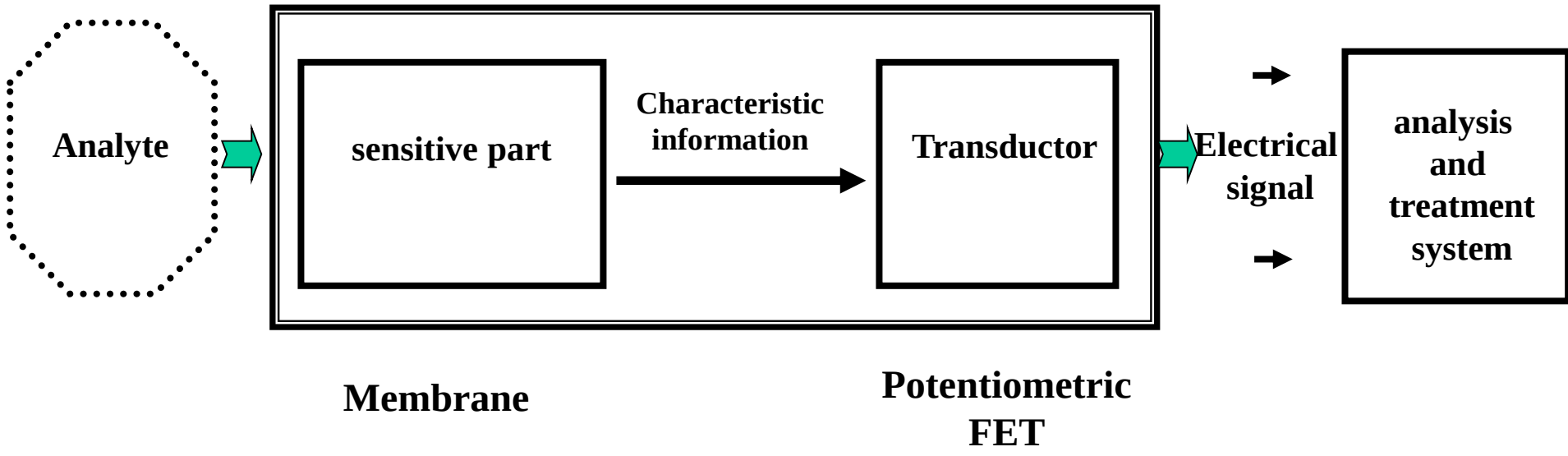
Application of ion diffusion in chalcogenide glasses

- Interface ion exchange
  - → Ion sensors
- Diffusion under $\vec{E}$
  - → Electrochemical energy storage : batteries
- Diffusion under photons hν
  - → Photoinduced phenomena
- Diffusion under $\vec{E}$ and hν
  - → PMC memories

Ion exchange : Chemical Sensor

Principle of a sensor

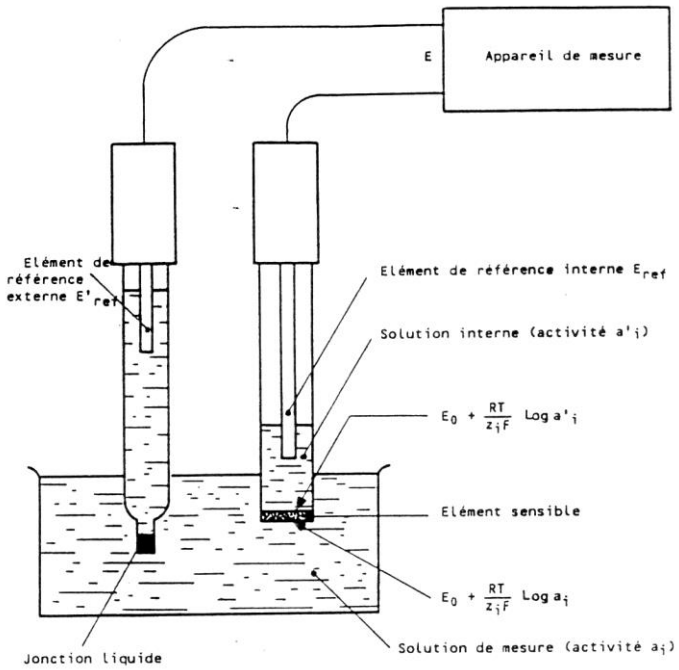
CHEMICAL or PHYSICAL SENSOR



Sensitivity, reversibility, selectivity and stability

Ion-selective electrode

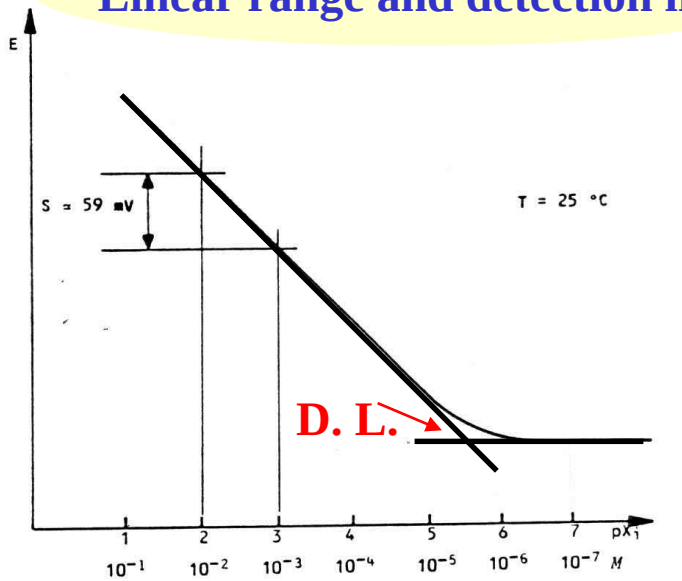
determination of e.m.f between the ISE and a reference electrode.



Potentiometric analysis of a chemical sensor depends on the relationship between the concentration of the species and the e.m.f. The ideal relationship is known as the Nernst equation :

$$E = E_0 + \frac{RT}{z_i F} \text{Log } a_i$$

Linear range and detection limit

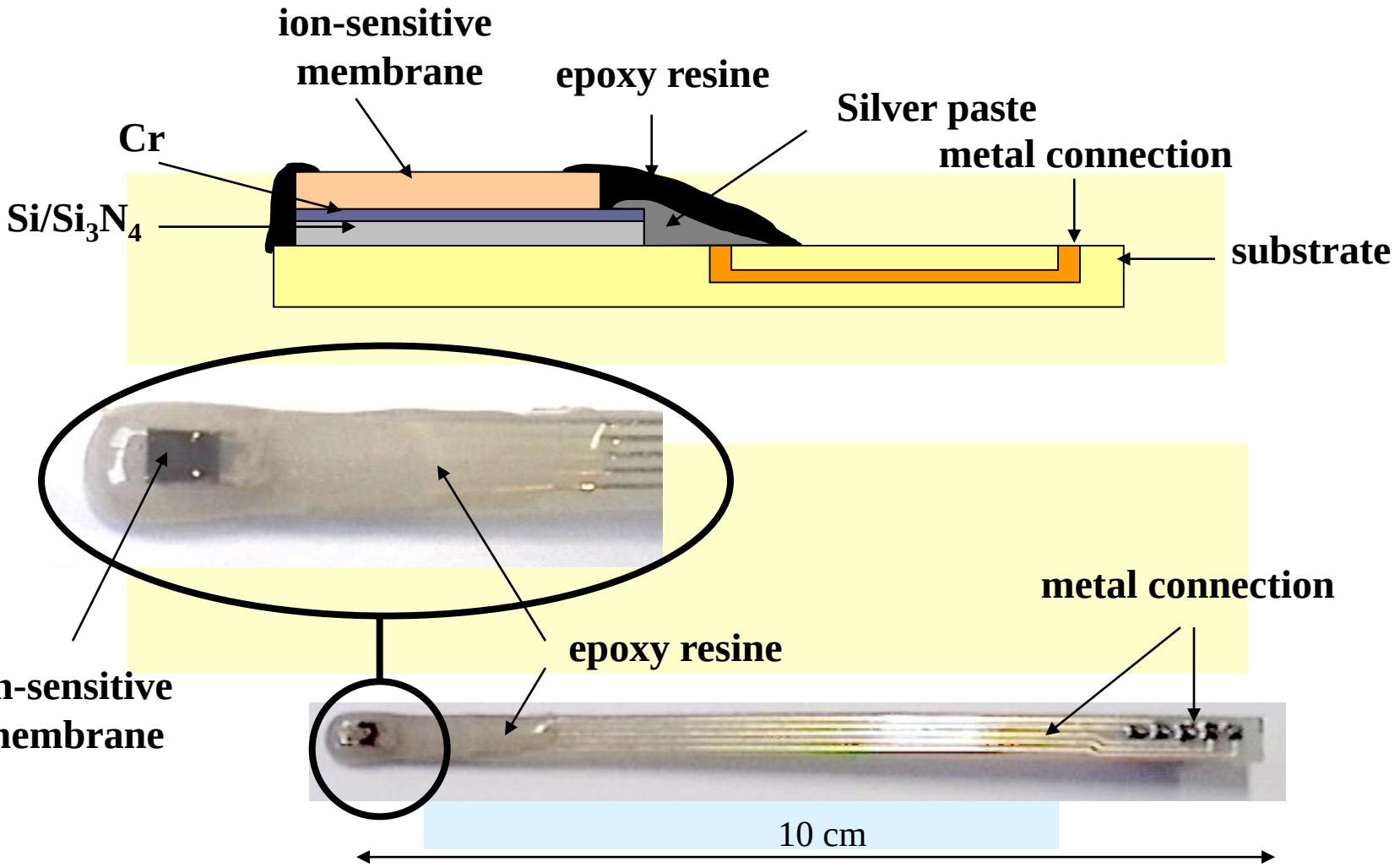


Slope of the response

Typical calibration curve of an ion-selective electrode obtained with the well known addition method.

Development of ISE chemical microsensors

Analytical device for Cu^{2+} ion detection based on $(1-X)Sb_{12}Ge_{28}Se_{60}$ – X Cu glassy thin films.

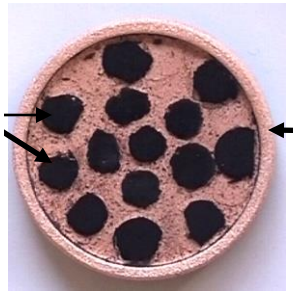


C.Cali,D.Foix,E.Siebert,D.Gombeau,A.Pradel, M. Ribes; Solid. State. Engineering C21 (2002) 3-8

Elaboration of the (Sb-Ge-Se)/(Cu) material

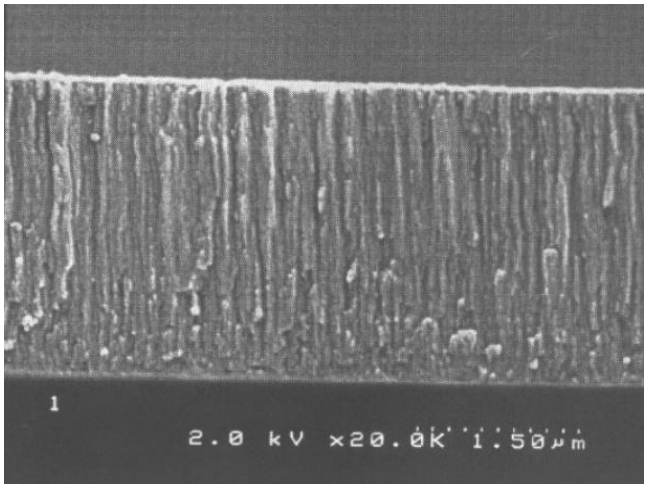
Thin films produced by r.f. sputtering of a composite target

$(Sb_{12}Ge_{28}Se_{60})$ → ← copper



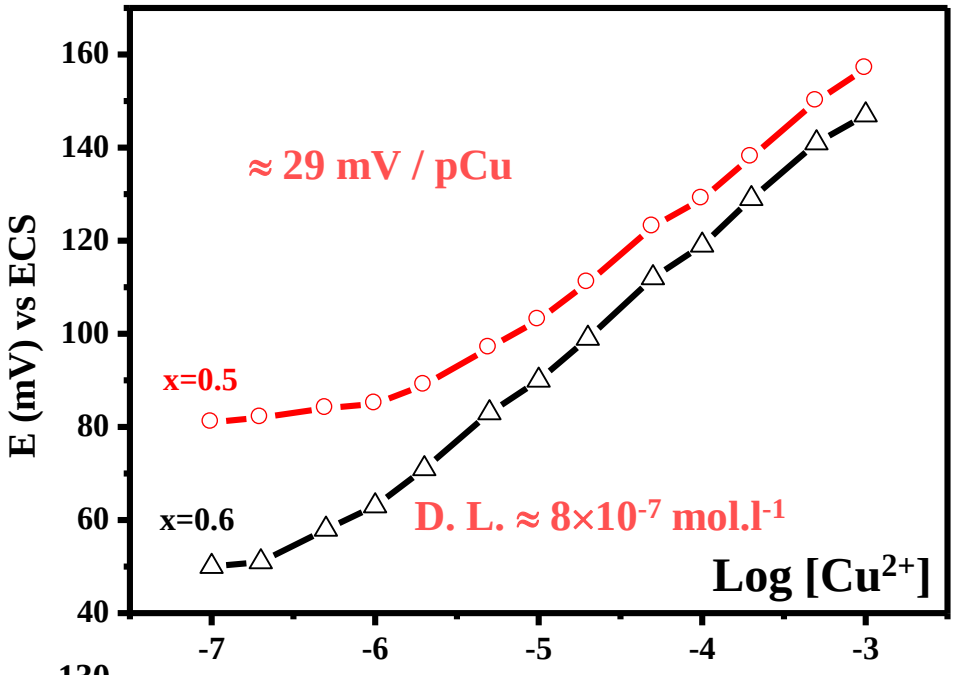
Target	Chemical composition of thin films
1	$(Sb_{11.3}Ge_{30.4}Se_{58.3})_{40}(Cu)_{60}$
2	$(Sb_{11}Ge_{29}Se_{60})_{50}(Cu)_{50}$

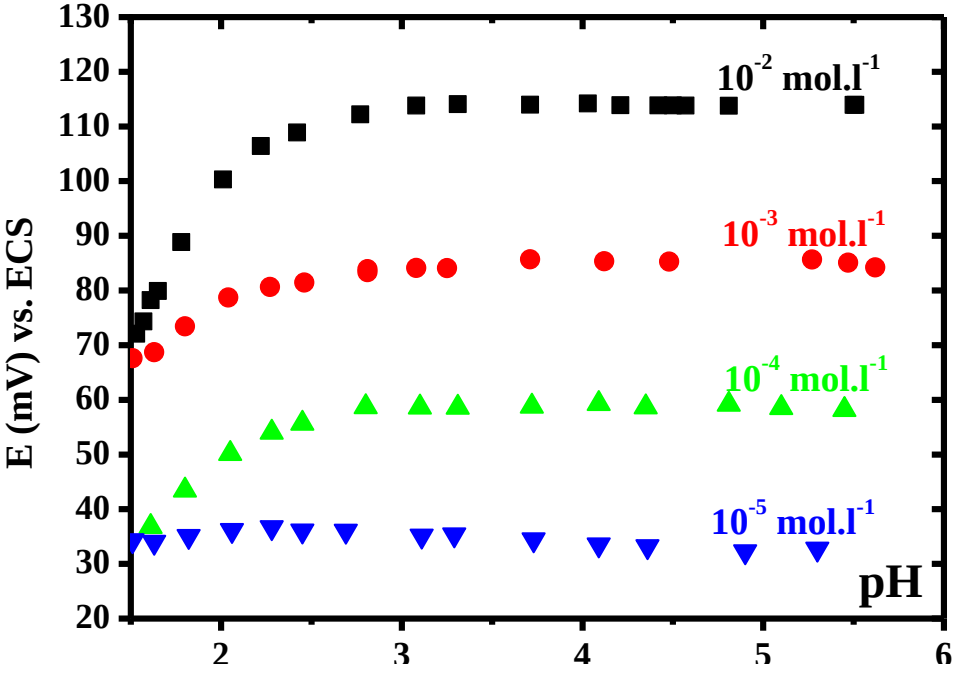
S.E.M cross sectional view of a thin film



Film thickness varies from 0.4 to 1 µm depending on sputtering conditions and sputtering time.

Electrode response





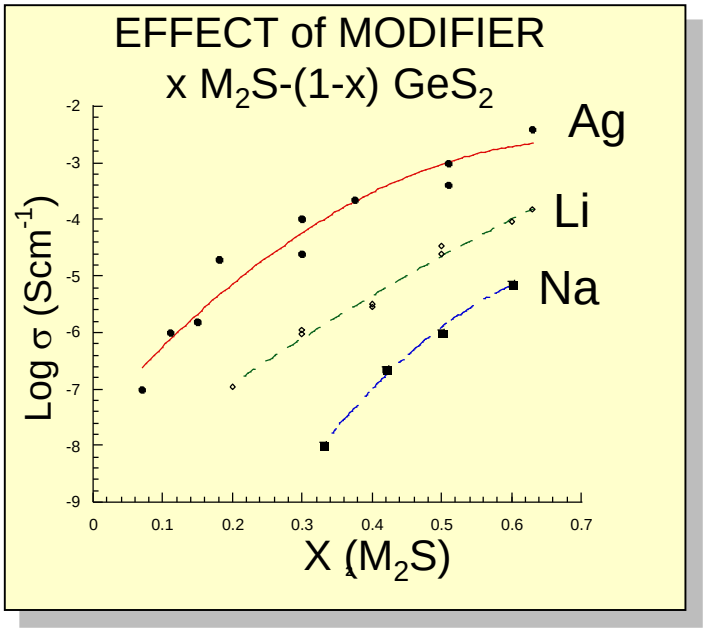
The material with x = 0.6 gives the best electrode performance.

Mixed solution method with constant a interfering ion concentration.

Interfering Ion	log $K_{Cu^{2+}/j}$
K^+	-5.1
Na^+	-5.3
Ca^{2+}	-5.1
Ni^{2+}	-4.1
Cd^{2+}	-4.1
Pb^{2+}	-2.5
Mn^{2+}	-3.4

Influence of pH on electrode response

Diffusion under $\vec{E}$: chemical energy storage



Superionic Conductive Glasses

Conductivity 100-1000 times larger than that of their oxide counterpart

ε_r > 10 (Weak electrolyte theory)

$\sigma_{Ag+} \sim 10^{-2}$ Scm^{-1}

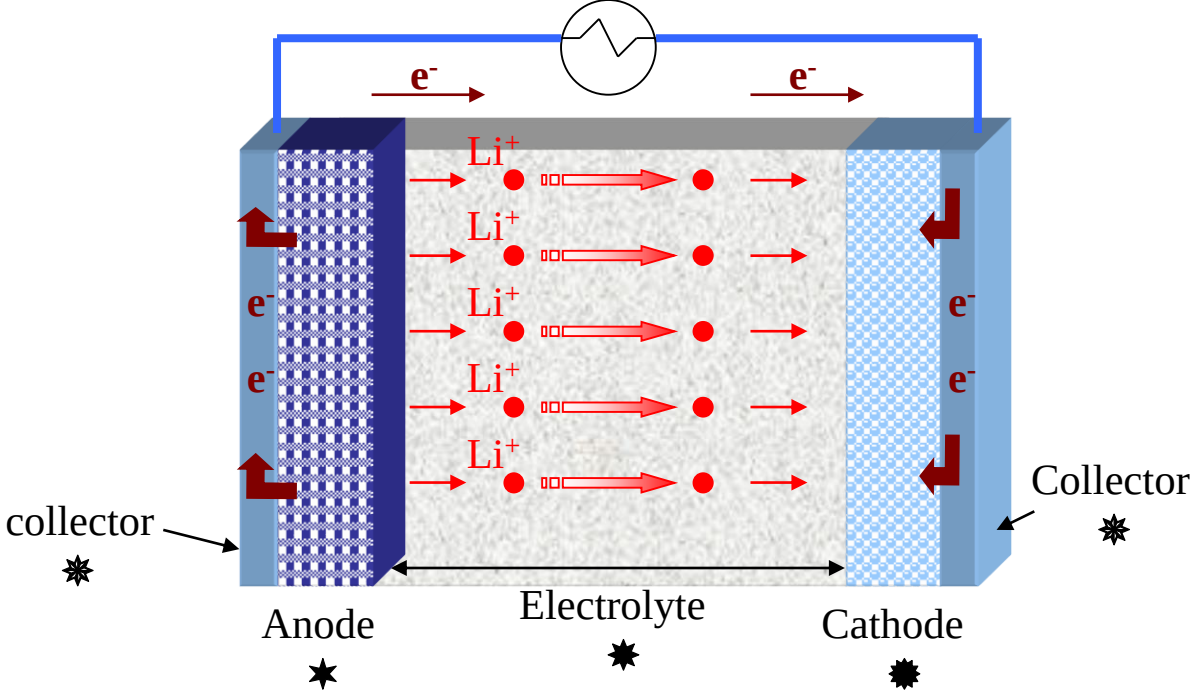
$\sigma_{Li+} \sim 10^{-3}$ Scm^{-1}

Application: all solid state batteries based on solid electrolytes

Rocking-chair Li-ion batteries for various portable equipments

- Safety: prevent from igniting and leaking (liquid combustible organic solvent)
- miniaturisation

Li-ion battery



At the begining: Li batteries

- **our first works (1983) $Li/LiI-Li_2S-GeS_2(g)/V_2O_5$**
- **Eveready (USA)(90 's) Li/ sulfide (oxysulfide) (g)/various cathodic materials**

Now Li-ion batteries (mainly japanese teams)

- **Minami-Tatsumisago group (Osaka)**
  $In/Li_2S-P_2S_5$glass-ceramics/$LiCoO_2$ (Chem.Letters 2002)
- **Takada et al (NIMS-Tsukuba)**
  $C/LiI-Li_2S-P_2S_5$ (g)//$Li_3PO_3-Li_2S-SiS_2$(g)/ $LiCoO_2$ (SSI 2003)

Li (or Li-ion) microbattery

Reduction of power supply of electronics devices

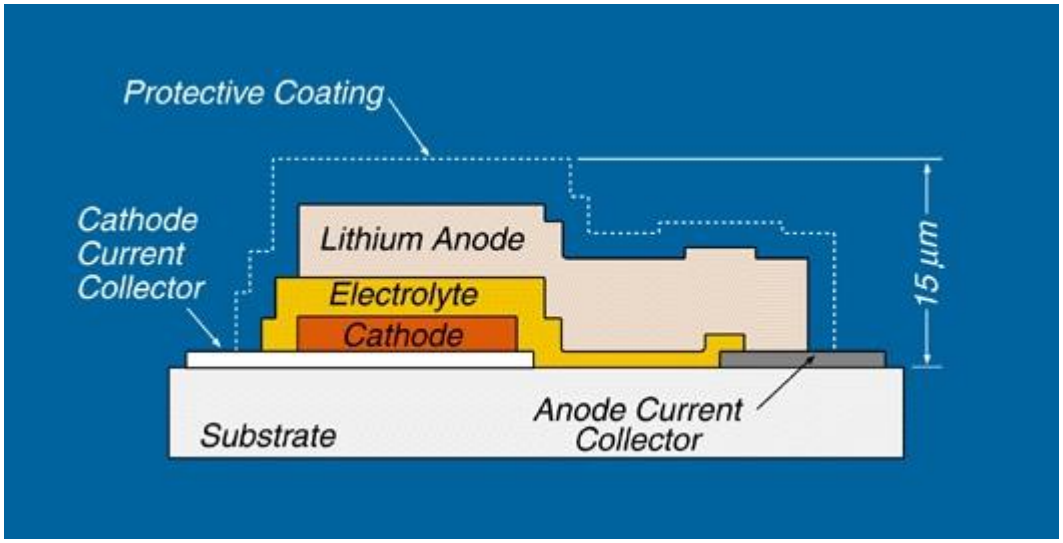
- Active power sources:

implantable medical devices, remote sensors, miniature transmitters, smart cards

- Standby power sources:

CMOS-SRAM memory devices (few $mWh.cm^{-2}$ are required to back up a CMOS memory chip)

Thin-films lithium battery developped at ORNL



Neudecker BJ, Dudney NJ and Bates JB ; J. Electrochem. Soc. 147 (2000) 517

Levasseur group Bordeaux Fr; Industrialization HEF Group (SVF Gazette du Vide 2 march 2003)

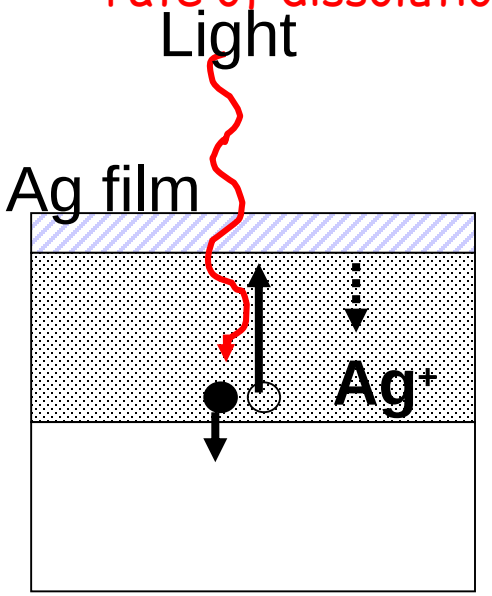
Diffusion under photons hν: Photoinduced phenomena

Photodissolution (« photodoping »)

Illumination of a chalcogenide film in contact with silver
-> rapid penetration of the metal into the semiconductor(Kostyshin (1966))

Typical features :

- large amount of Ag can be dissolved 30-40 at%, and even 57% in GeS_3
- rate of dissolution depends on chalcogenide composition (excess in chalcogen)



Mechanism

ionization of Ag

(semiconductor → presence of holes or electrons)

$Ag + h^+ \rightarrow Ag^+$ $\qquad$ $Ag \rightarrow Ag^+ + e^-$

reduction of chalcogenide

$2Ag + Se \rightarrow Ag_2Se \quad \Delta G^\circ_{298} \sim -25$ kJ/mol

$4Ag + 2As_2Se_3 \rightarrow 2Ag_2Se + As_4Se_4 \quad \Delta G^\circ_{298} \sim -12$ kJ/mol

hν close to bandgap energy

Photo-enhanced solid state reaction

T. Kawaguchi, K. Tanaka and S.R.Elliott; Handbook of advanced electronic and photonic materials and devices AP, N.H Nalwa ed. (2001) p 91

Application of photodissolution

- Very sharp edges between doped and undoped regions

Local creation of pairs « electron-hole » + small diffusion length of free carriers

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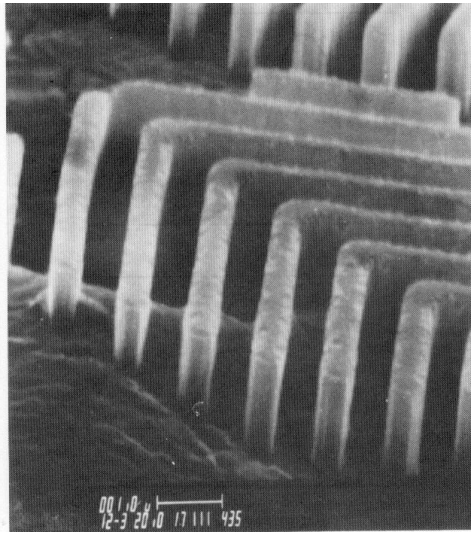
Hardly any lateral diffusion

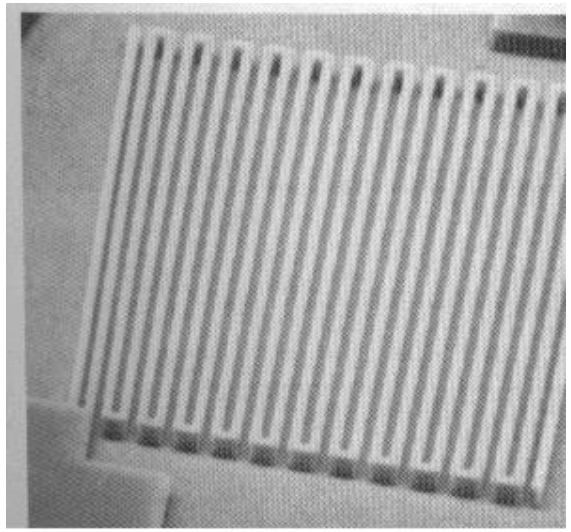
- Solubility of doped region in alkaline solvents much reduced

Local change in chemical composition

photoresists ⟶

etched gratings





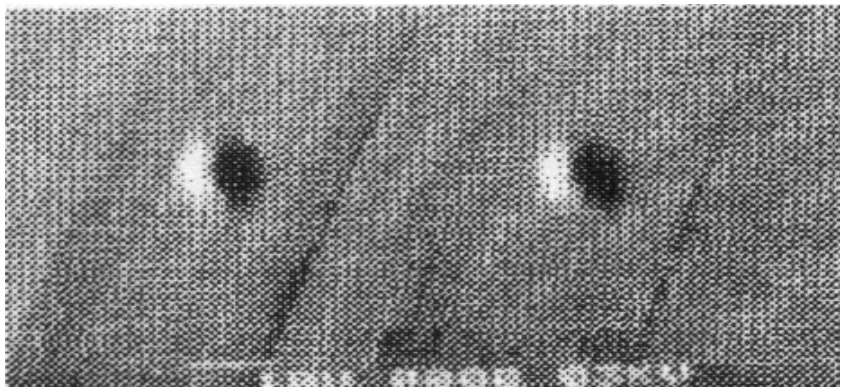
Photomigration - Photodeposition

Phenomenon observed in highly doped chalcogenide: Ag-Ge-S(e), Ag-As-S(e). For example in $(Ge_{0.3}S_{0.7})100\text{-}xAgx$ films when $x > 0.45$

Illumination

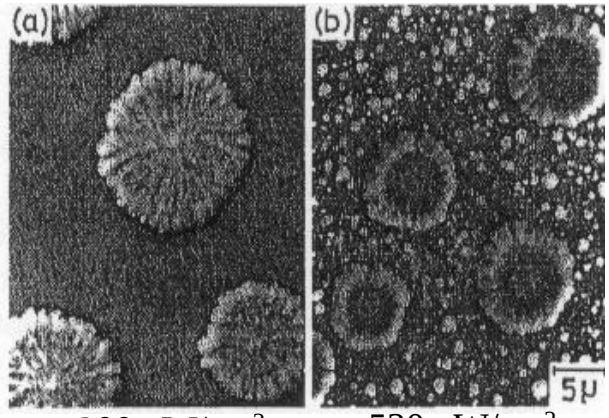
lower silver content ($x < 0.45$)

increase in Ag density
in the illuminated part



higher silver content ($Ag_{45}As_{15}S_{40}$)

precipitation of Ag



200mW/cm^2 530mW/cm^2

Small clusters or crystals
10nm in diameter and 1nm in thickness

Reversible process

Annealing $\rightarrow$ dissolution of the Ag clusters

T. Kawaguchi et al JNCS 212 (1997) 1666

Mechanism of photomigration-photodeposition

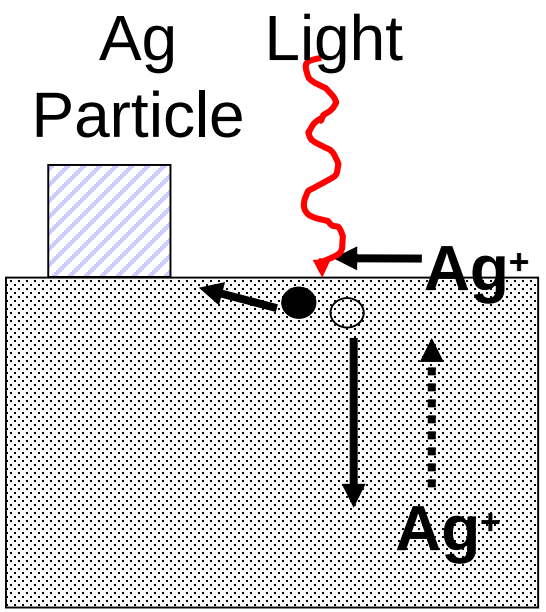
Point of view of physicist

Illumination

creation of pair « electron-hole »

$Ag^+ + e^- \rightarrow Ag$

h^+ moves away from illuminated spot



Point of view of chemist

Photodecomposition = decomposition of an oversaturated Ag solid solution

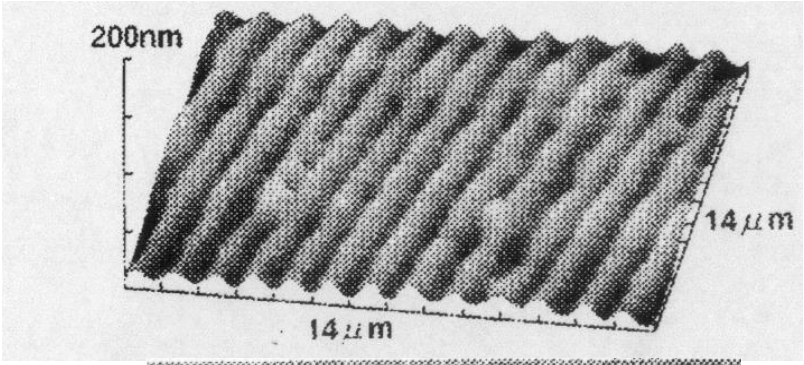
Under illumination the metastable system approaches equilibrium with excess Ag segregation.

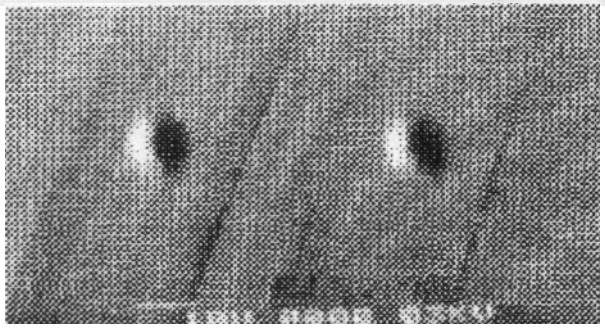
Annealing at higher temperature allows Ag to dissolve again in the solid solution

Application of photomigration-phodeposition

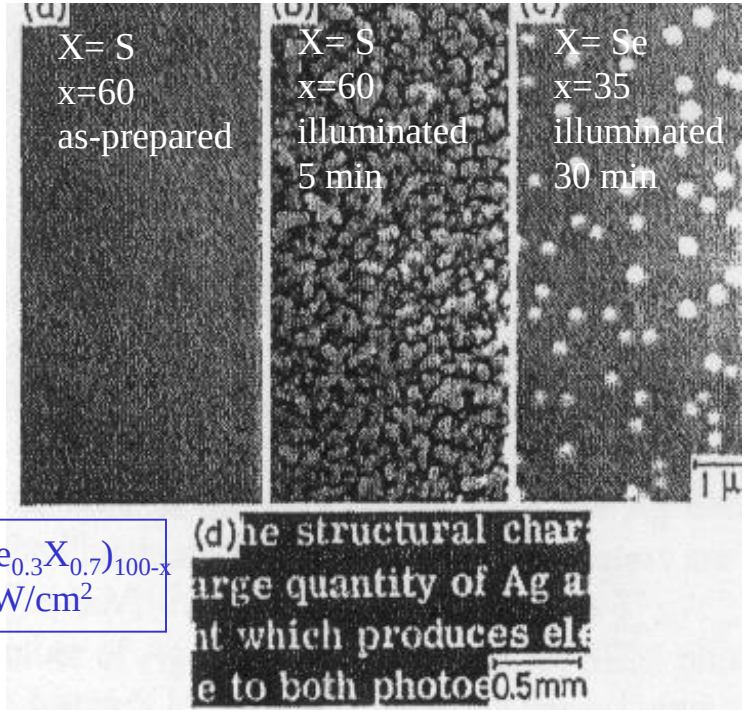
- Increased reflectivity for Ag rich region
- photoexpansion

Gratings/ microlenses





Optical memories



$Ag_x(Ge_{0.3}X_{0.7})_{100-x}$
110 mW/cm^2

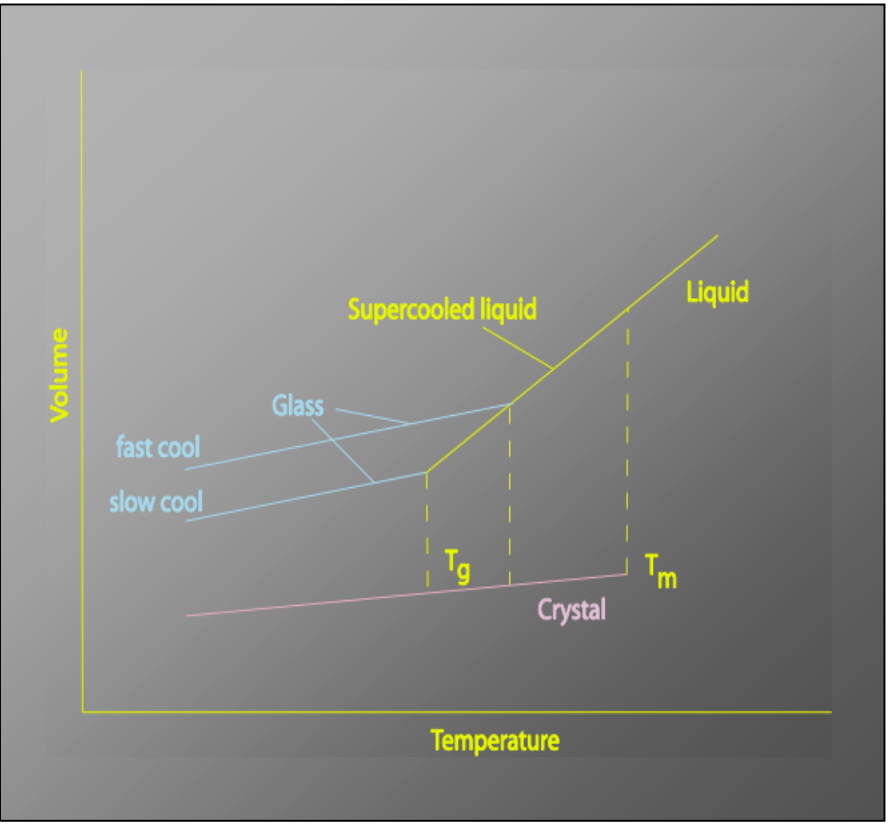
Au addition → increase in the photosensitivity of photodeposition by two orders of magnitude (Au clusters = nucleation centers for Ag)

T. Kawaguchi, K. Tanaka and S.R.Elliott; Handbook of advanced electronic and photonic Materials and devices AP, N.H Nalwa ed. (2001) p 91

Photocrystallisation (phase change)

Exist in chalcogenide with or without ion

- Ge-Sb-Te (GST-$Ge_2Sb_2Te_5$)
- Ag-In-Sb-Te (AIST)



Ordered state

crystalline $AgSbTe_2$ + amorphous In-Sb

Disordered state

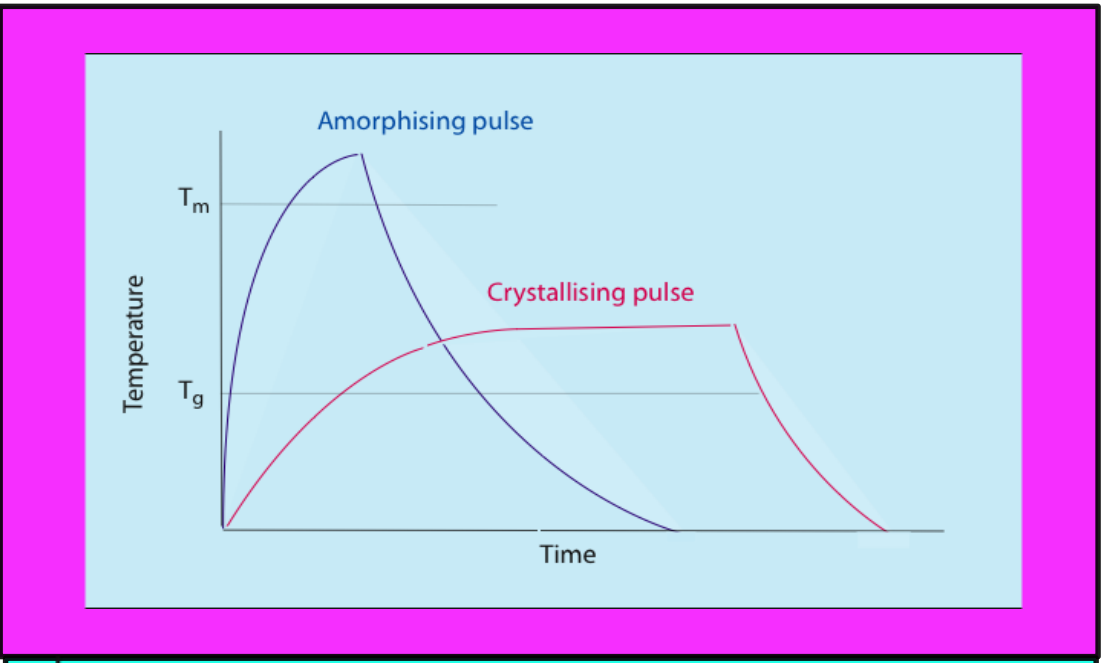
amorphous $AgSbTe_2$ + amorphous In-Sb

$h\nu$
laser beam

Critical cooling rate
3.4 K/ns

Different reflectivity for amorphous and crystalline $AgSbTe_2$

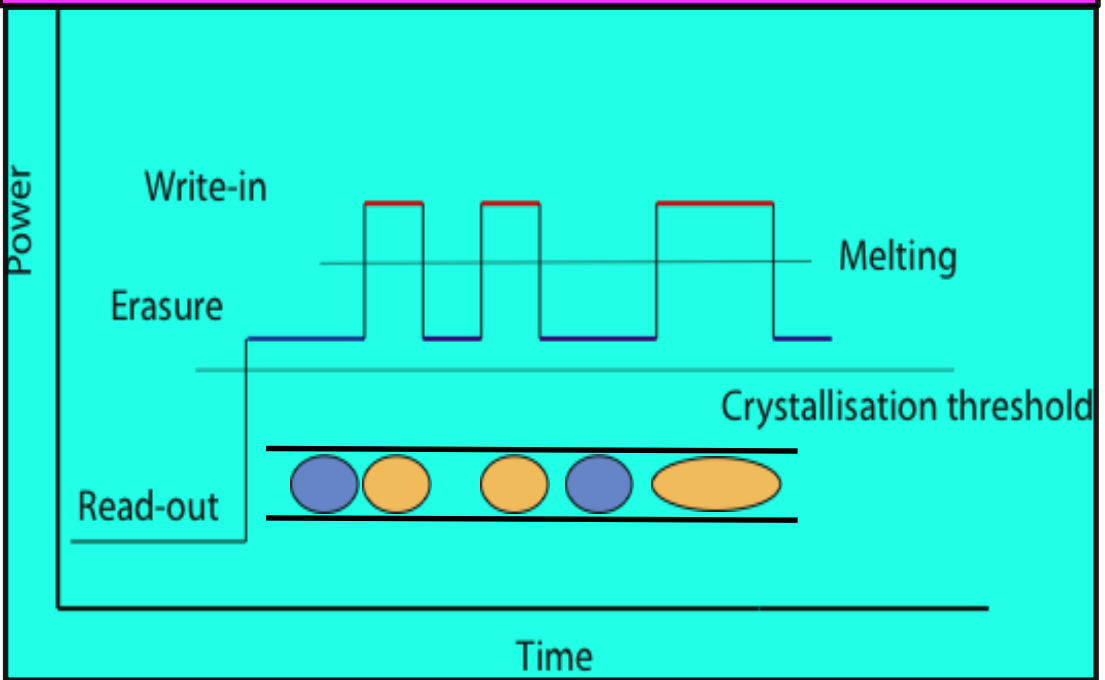
Application of photocrystallisation



Rewritable optical disk memory

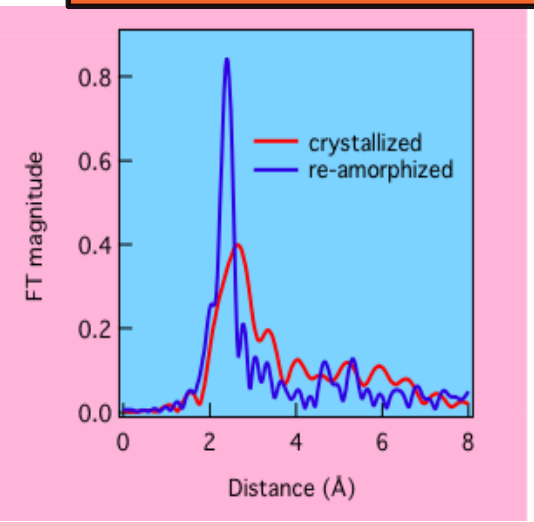
Phase change: Write/Erase phenomena

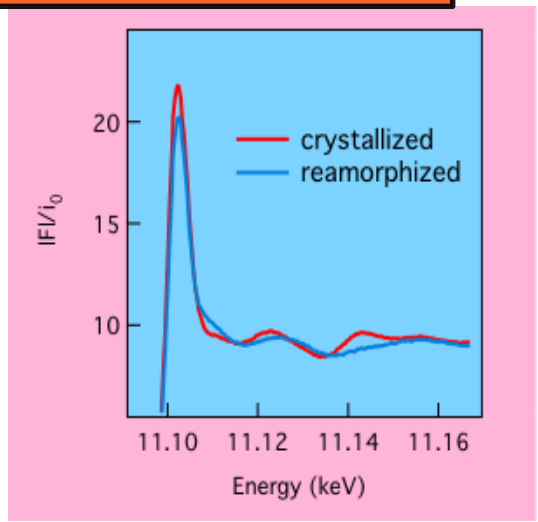
Laser-induced annealing/melting



Pulse structure

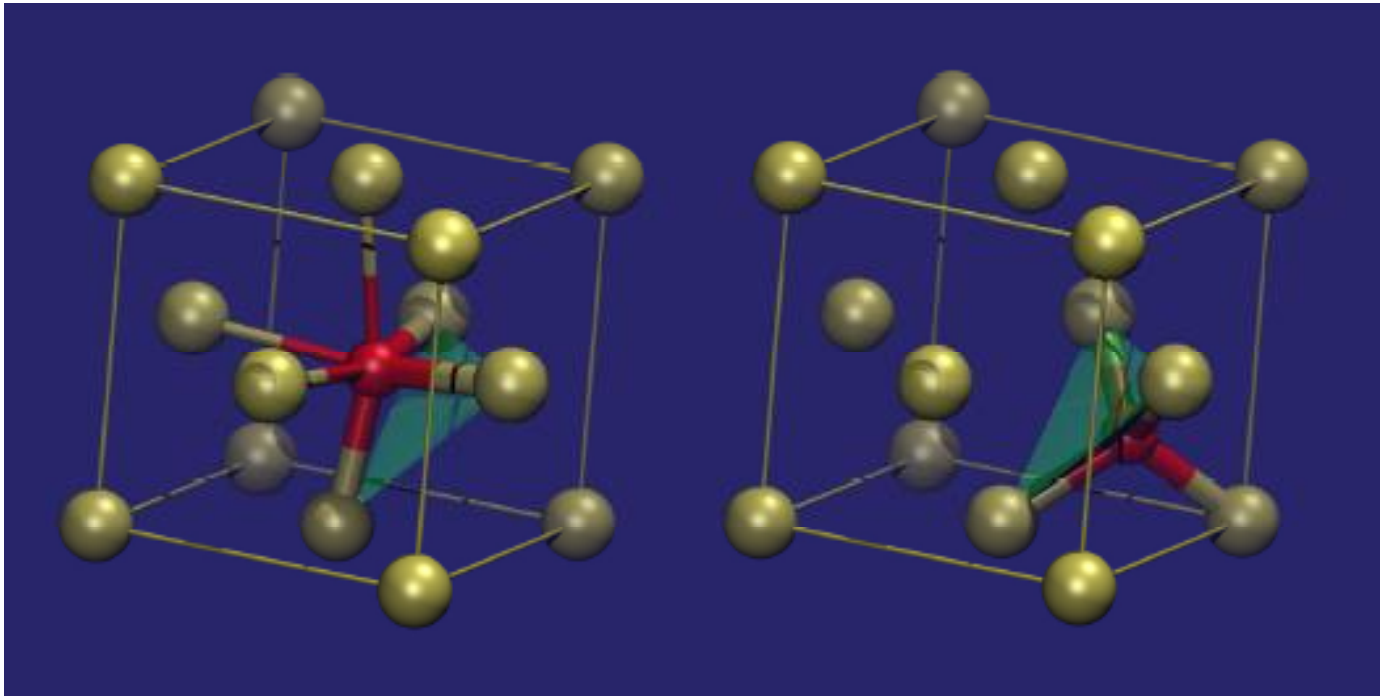
Ge-edge data ($Ge_2Sb_2Te_5$)





The transition between the crystalline and amorphous states can be viewed as an umbrella-switch of Ge atoms from a octahedral to tetrahedral symmetry position within the Te fcc sublattice

Very big change in EXAFS and XANES



A.Kolobov et al, 2004, Nature Mater. 3, 703

Real disc structure

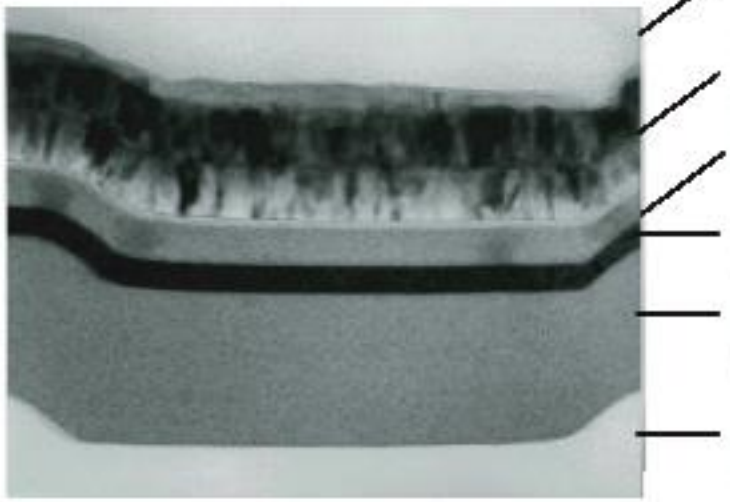


Fig. 6. Cross-sectional TEM observation of the basic 4-layer phase-change optical disk.

UV resin

Reflection layer (heat sink)

Protection layer ZnS-SiO_2

Active layer (GST, AIST)

Protection layer ZnS-SiO_2

Polycarbonate disc

T. Ohta, JOAM 2001

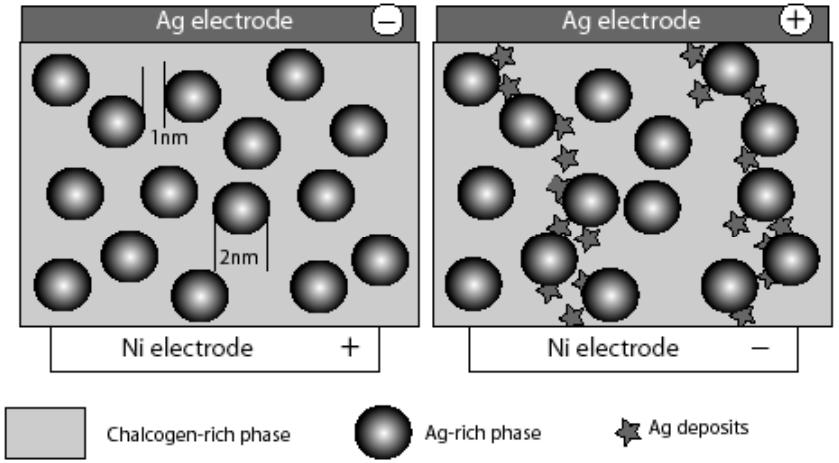
WHY PHOTOSTRUCTURAL CHANGES OCCUR ONLY IN AMORPHOUS CHALCOGENIDES?

- Excitation of lone-pair electrons is a trigger of the structural change - presence of LP-electrons is crucial - group VI elements (chalcogens);
- Localization of photo-excited carriers and hence disorder is important - amorphous;
- Low coordination number is beneficial since it makes the structure floppy.

Amorphous chalcogenides are the only materials that satisfy all these requirements

Diffusion under $\vec{E}$ and hν : PMC memories

« Programmable Metallization Cell Memory Devices »

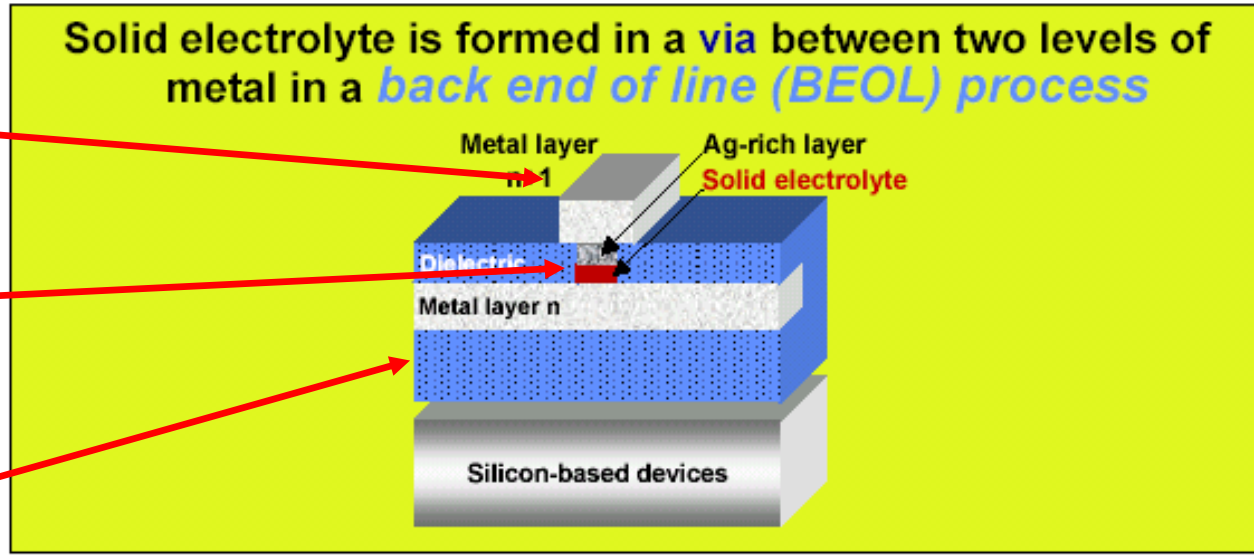


- *bias* → accumulation of silver metal creating a conductive link (« on » state) -Ag is oxidised at the anode and reduced at the cathode
- Reversing the *bias* breaks down the silver and restore the initial resistive state (« off » state)

Anode: Ag
or Ag-containing material

Solid electrolyte:
Ag photodissolution
in GeS(Se)y

Cathode: inert metal
(Cr,Ni..)



M. N. Kozicki, M. Mitkova, M. Park, M. Balakrishnan, C. Gopalan, *Superlattices and Microstructures* 34 (2003) 459.

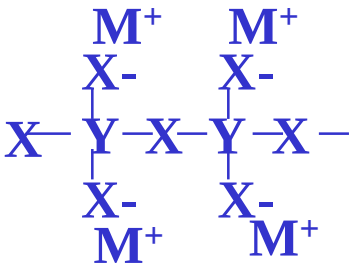
Ionic conductive chalcogenide glasses

Glasses exist in large composition domains

Former YX_2 (Y = Si, Ge…X = S, Se) — Covalent bonds

\+

Modifier M_2X (M = Li, Na, Ag..) — Ionic bonds



(Glass)

Ag (Na)- based chalcogenide glasses

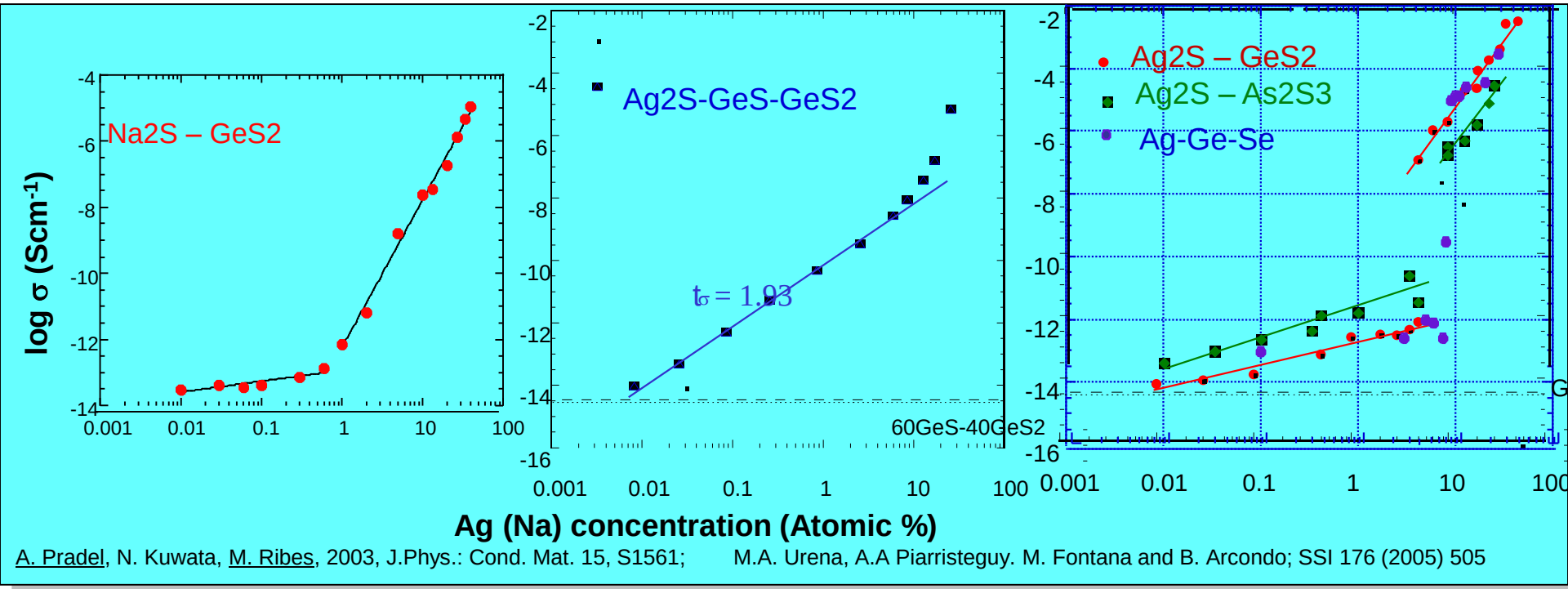
Ag_2S - GeS_2
Ag_2S – GeS - GeS_2
Ag_2Se - $GeSe_2$*
Ag_2S - As_2S_3
Na_2S - GeS_2

Ag (Na) content varying from 0.01 - 30 at%

→ evolution of conductivity with composition
→ non-Arrhenius behaviour ($\log \sigma \propto 1/T$)

*M.Kawasaki, Kawamura J, Y. Nakamura and M. Aniya; SSI 123 (1999) 259
M.A. Urena, A.A Piarristeguy. M. Fontana and B. Arcondo; SSI 176 (2005) 505

Variation of conductivity (298 K) with Ag(Na) content (at %) in Ag(Na)-X-Y glasses (X=Ge,As; Y=S,Se)



A. Pradel, N. Kuwata, M. Ribes, 2003, J.Phys.: Cond. Mat. 15, S1561; M.A. Urena, A.A Piarristeguy. M. Fontana and B. Arcondo; SSI 176 (2005) 505

3 different behaviours

- Na2S-GeS2 : Change in the transport regime at about 1 at % in sodium (electronic to ionic ?)
- Ag2S-GeS-GeS2 and Ag-based glasses: Change in the transport regime at about 5-8 at % in silver
- Ag-based glasses:large increase of 4-5 orders of magnitude in the conductivity at about 5-8 at % in silver

Ag2S-GeS-GeS2 and Ag-based glasses
Structural studies (microscopic, nanoscopic scale)

FE-SEM (Field Effect - Scanning Electron Microscopy)

Chemical inhomogeneities

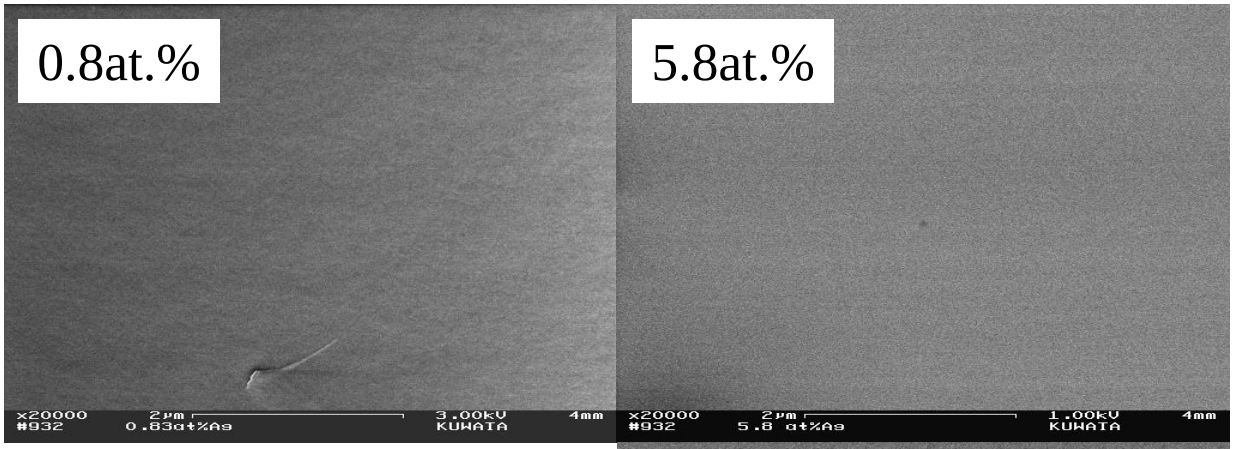
EFM (Electric Force Microscopy) Surface potential imaging and surface electric modification

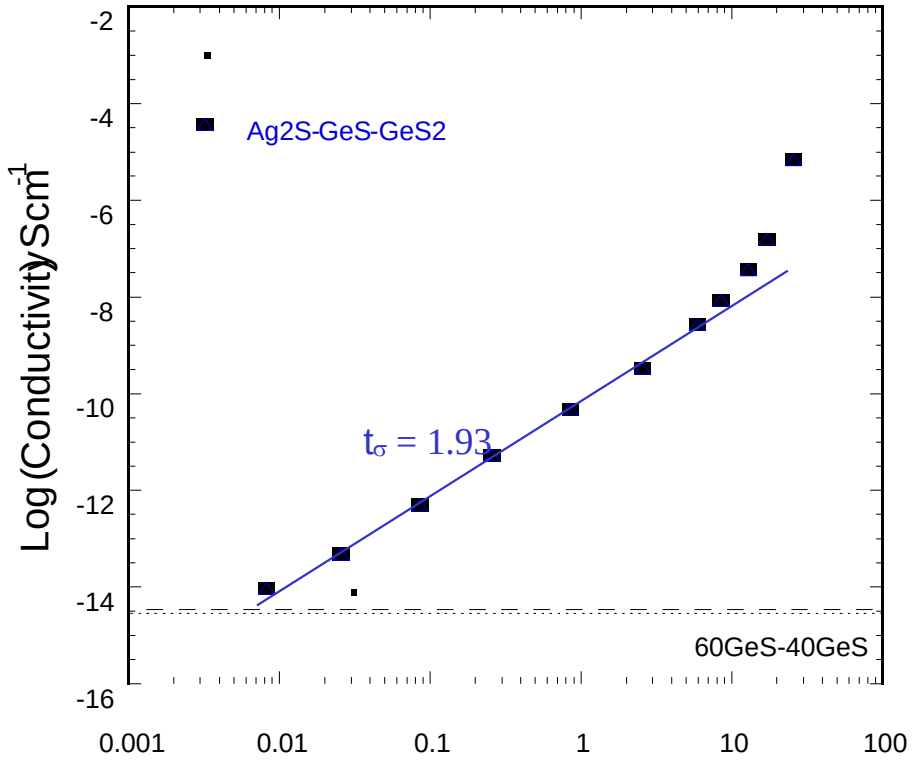
Electrical inhomogeneities

FE-SEM
(LEO-982)

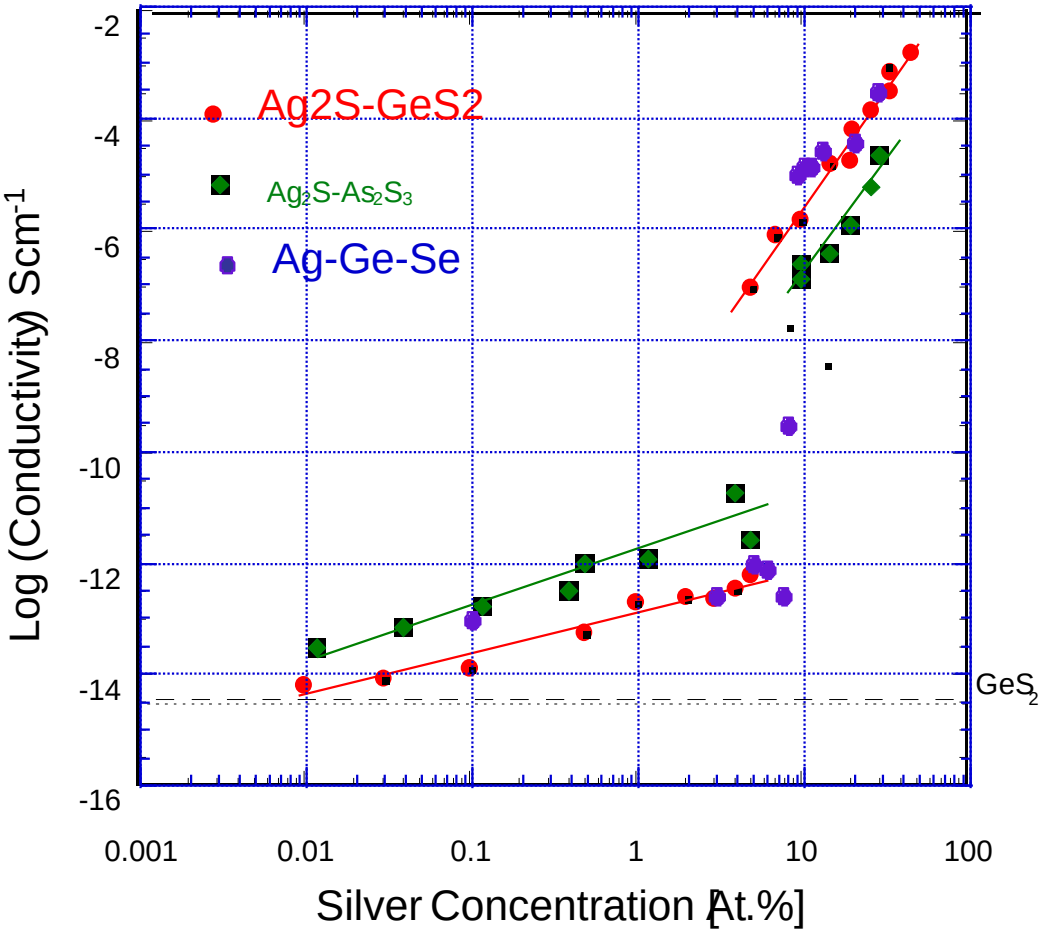
Ag_2S-GeS-GeS_2

No phase separation





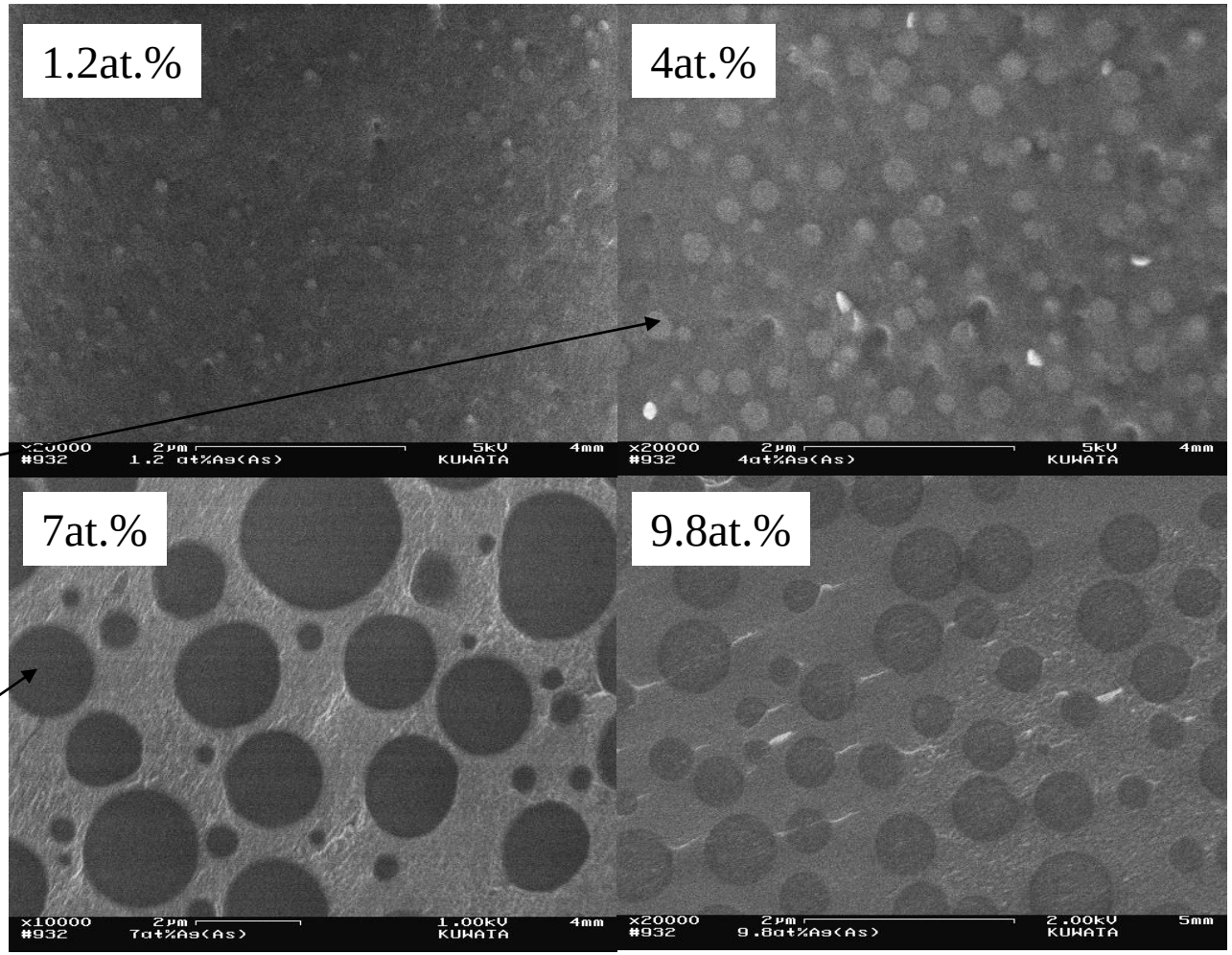
Ag-based glasses showing a large increase (4-5 orders of magnitude) in the conductivity at about 5-8 at % in silver



FE-SEM
(LEO-982)

$Ag_2S - As_2S_3$

Glasses are phase separated



Ag-rich phase

Ag-poor phase

the change in the conductivity regime occurs when the Ag-rich phase starts connecting

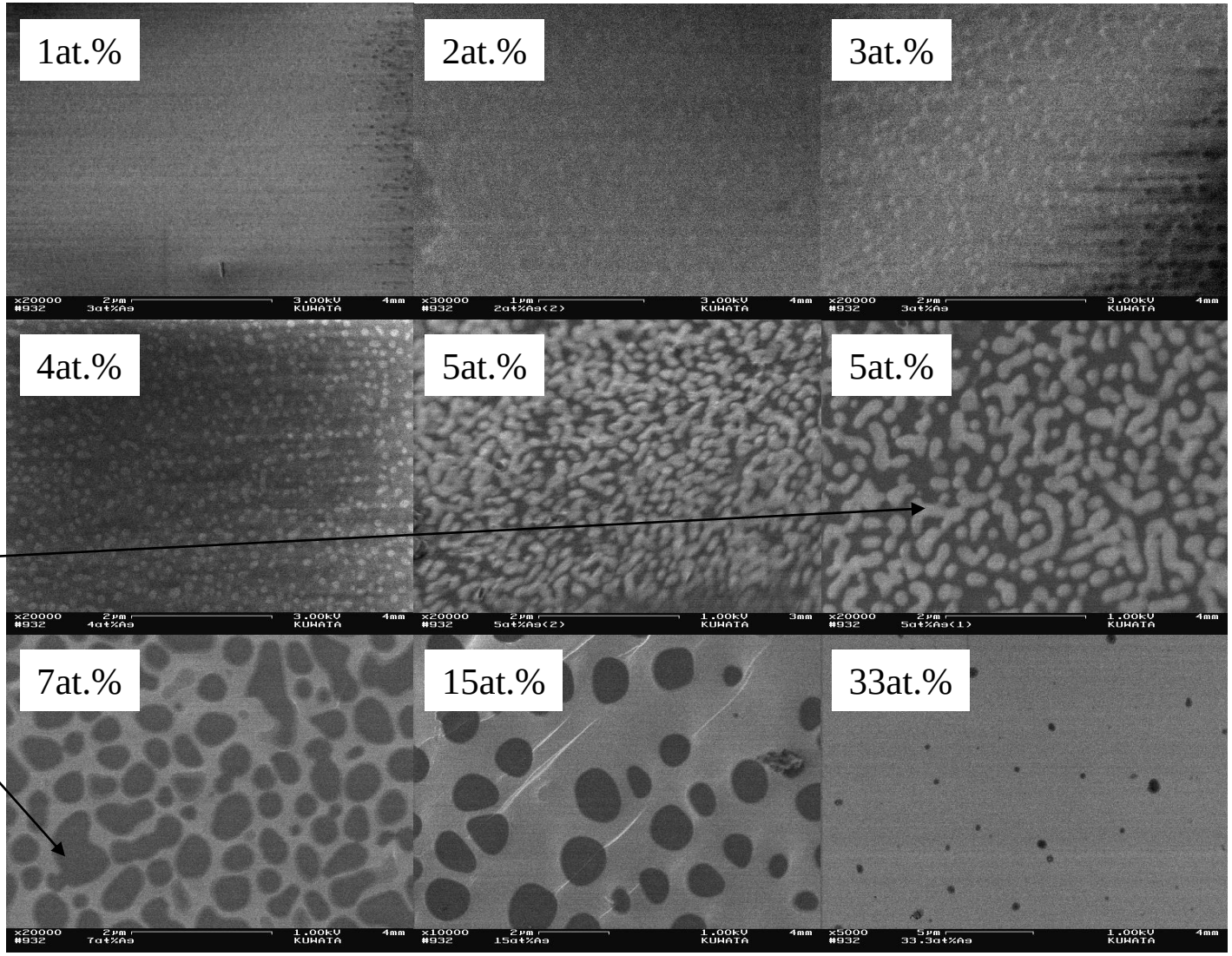
FE-SEM
(LEO-982)

$Ag_2S - GeS_2$

Glasses are phase separated

Ag-rich phase

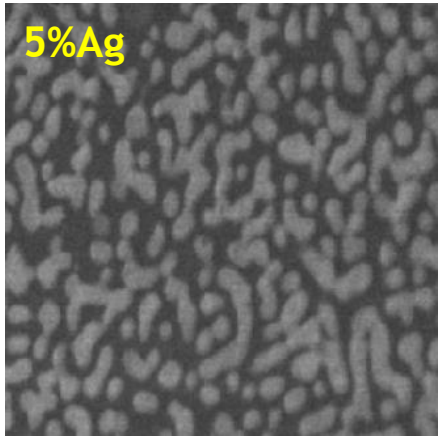
Ag-poor phase



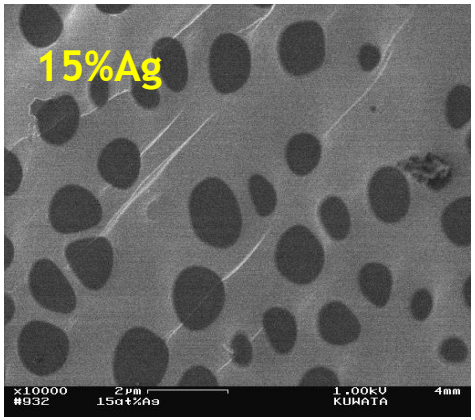
the change in the conductivity regime occurs when the Ag-rich phase starts connecting

Comparison FE-SEM / EFM (Ag2S-GeS2 glasses)

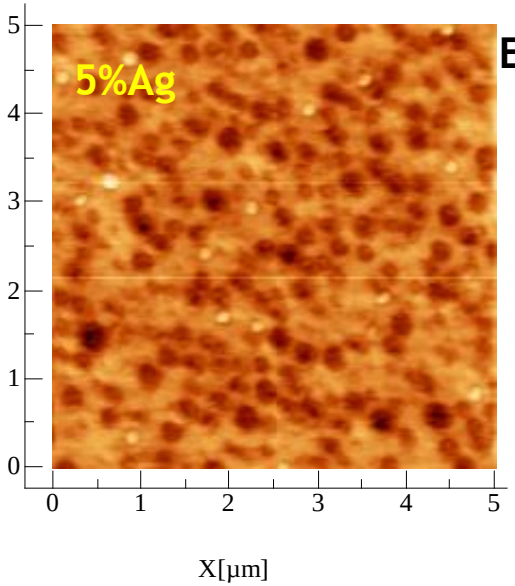
- Weak conductivity domain : Ag-poor phase connected
- High conductivity domain : Ag-rich phase connected



Clear areas (Ag-rich phase) d~0,3µm

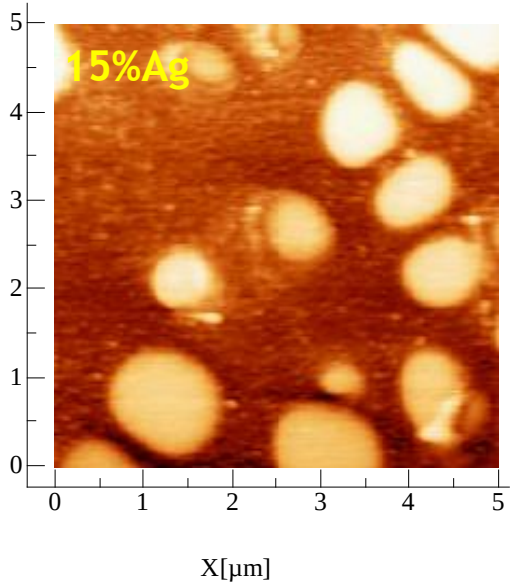


Dark areas (Ag-poor phase) d~0,8-0,9µm



EFM -3V

Dark areas (Ag-rich phase)

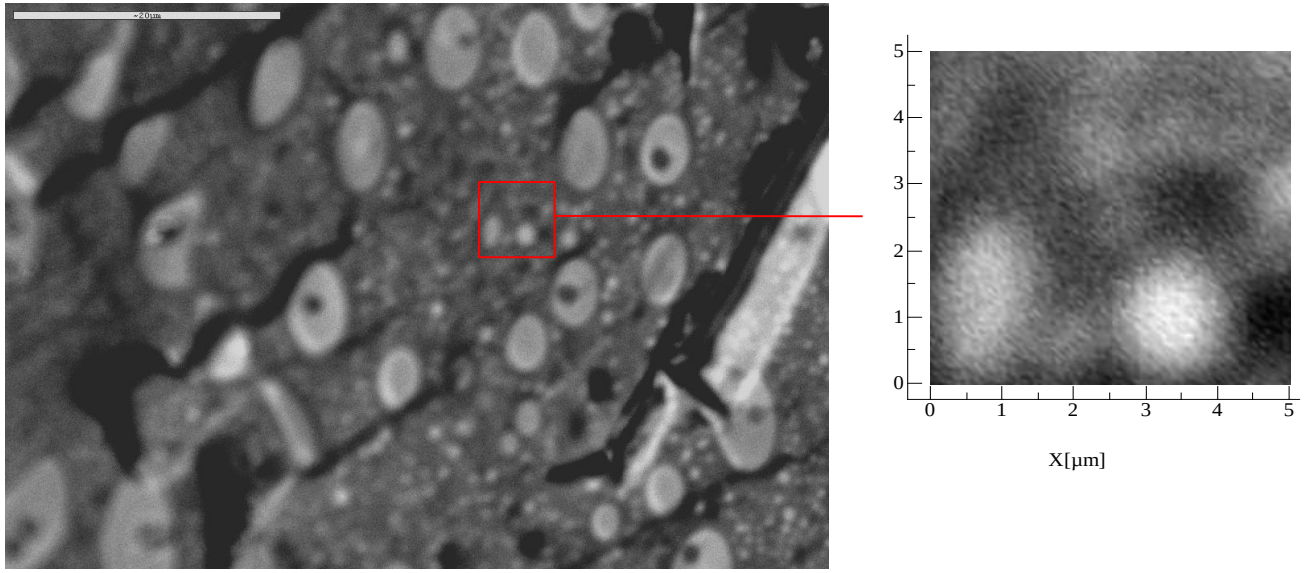


EFM -3V

Clear-areas (Ag poor phase)

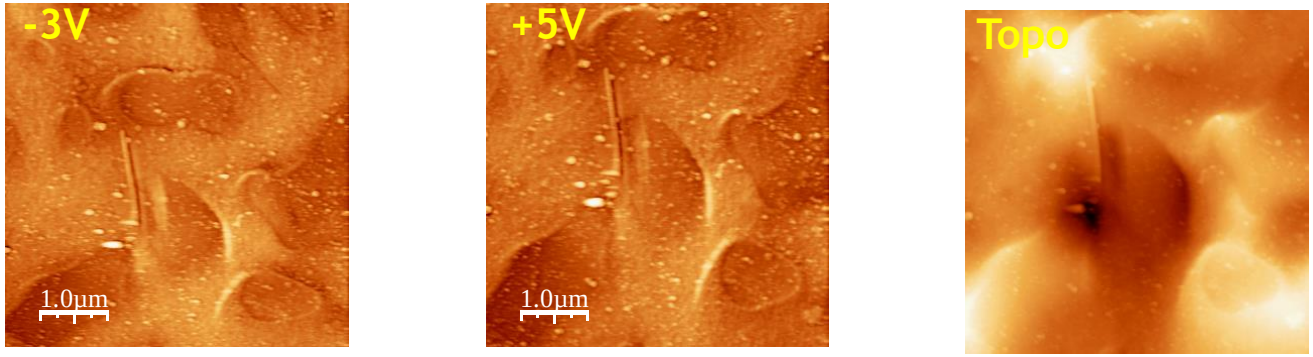
$(Ge_{25}Se_{75})Ag{:}10\%$

Electrons retrodiffusés



Clear areas (Ag-rich phase in a Ag-poor matrix)

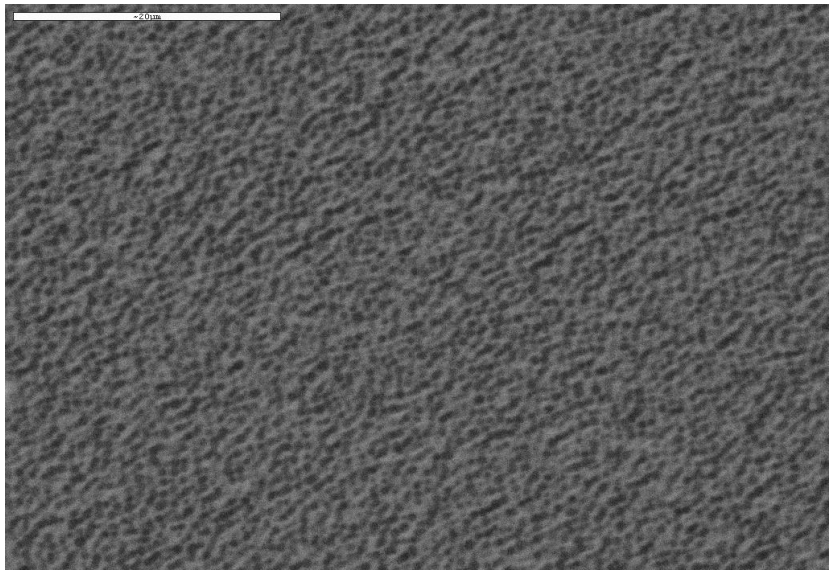
EFM

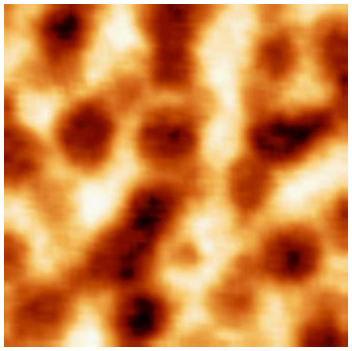


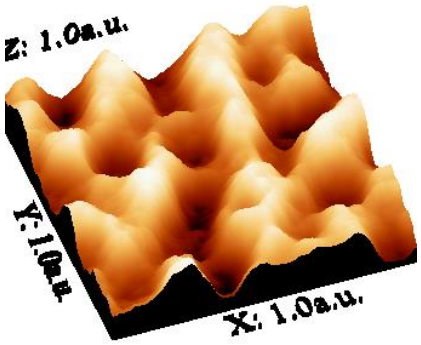
Dark areas in a clear matrix but a weaker contrast !

$(Ge_{25}Se_{75})Ag{:}15\%$

Electrons retrodiffusés

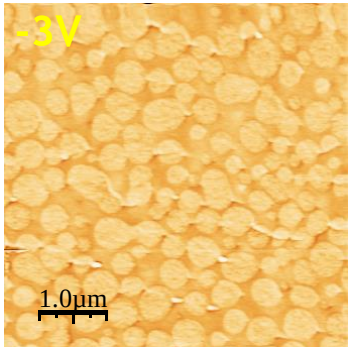


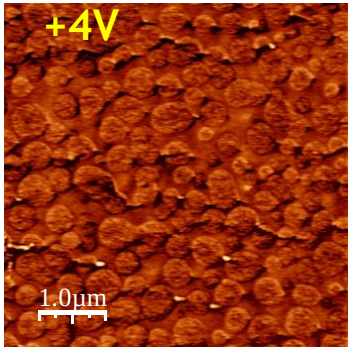


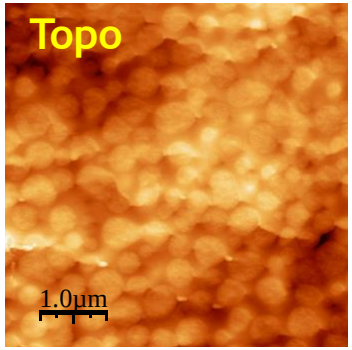


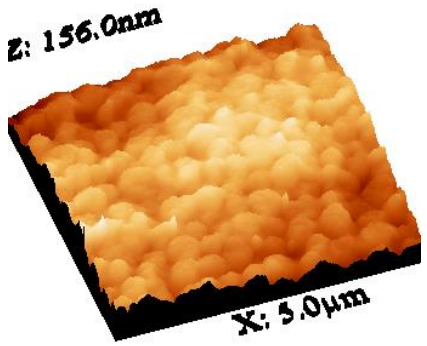
d~1µm

EFM



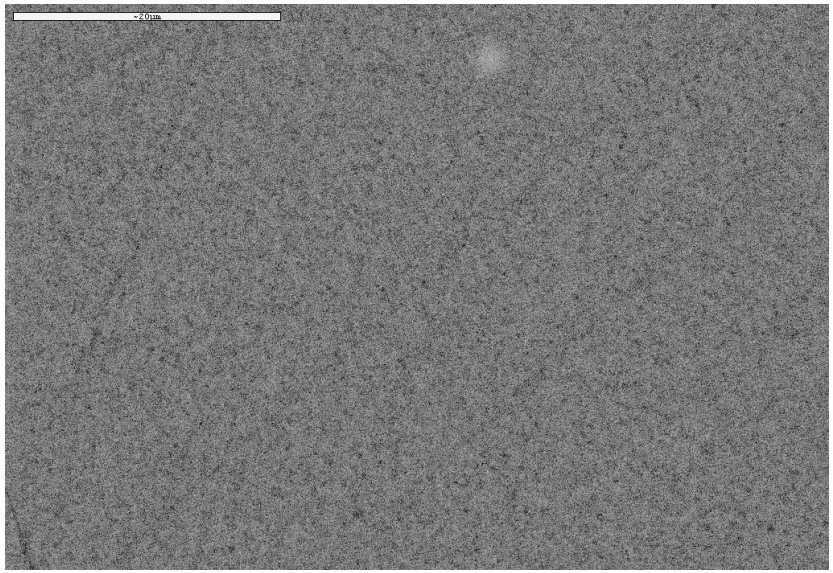


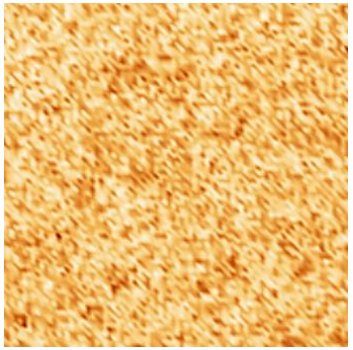


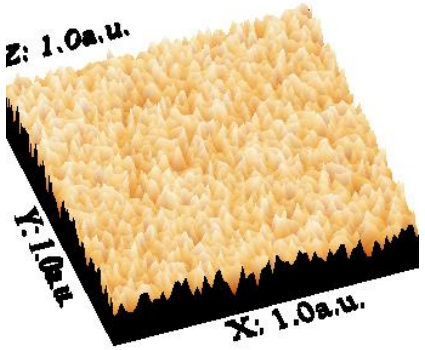


$(Ge_{25}Se_{75})Ag:25\%$

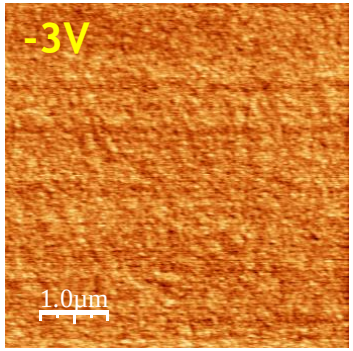
Electrons retrodiffusés

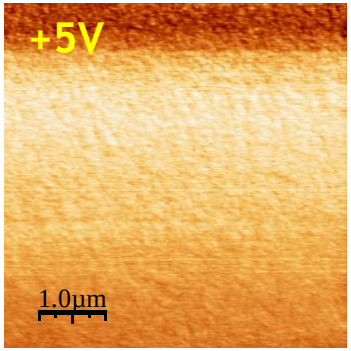


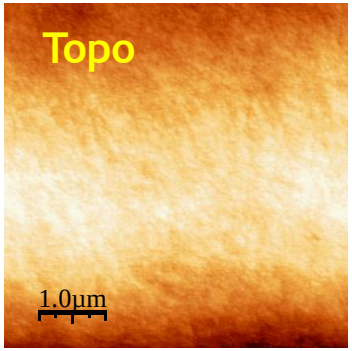


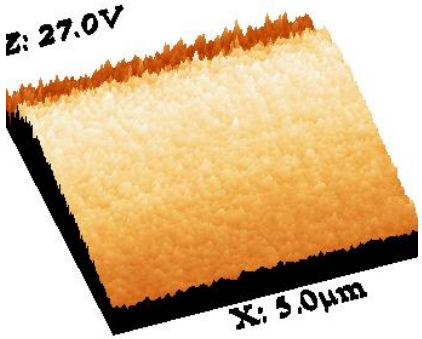


EFM

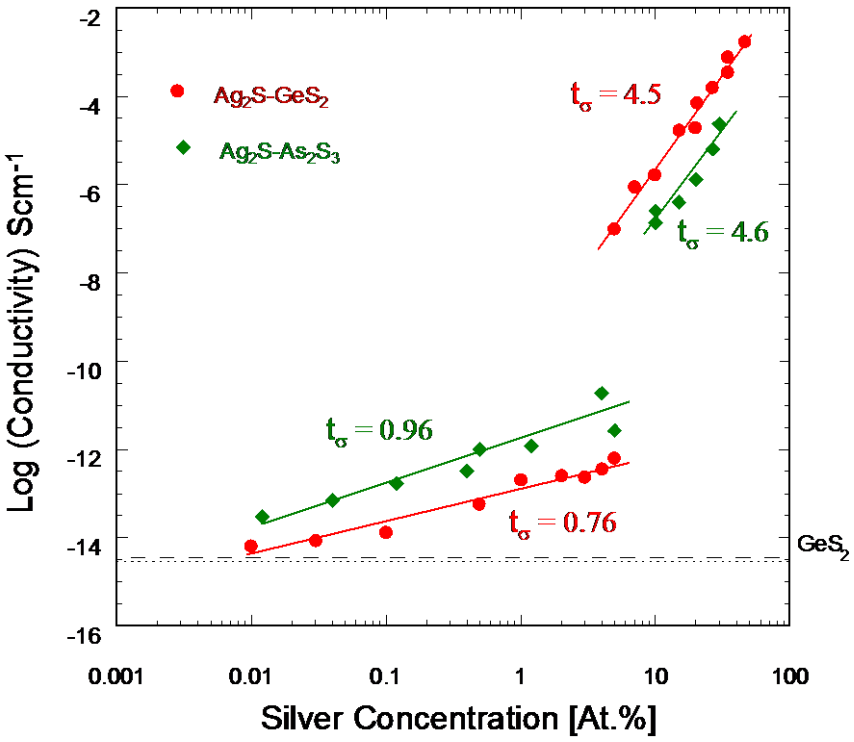








Variation of conductivity (298 K) with Ag content (at %) in Ag_2S - GeS_2 and Ag_2S - As_2S_3 glasses



The glasses are phase separated

The jump in the conductivity occurs when the phase previously embedded in the connecting phase becomes the connecting one

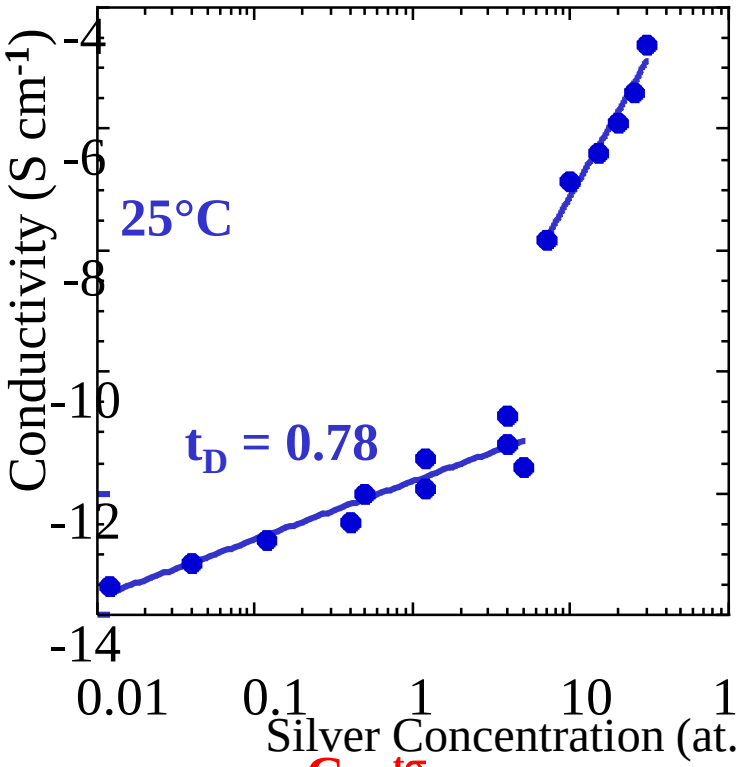
percolation threshold with the Ag-poor phase (Ag-rich phase) being responsible for the conductivity at low silver (high silver) content

At low Ag content, power law dependence: $\sigma = Cx^{t\sigma}$

Nature of the charge carriers (electrons to ions)?
EMF <---> Tracer diffusion coefficient

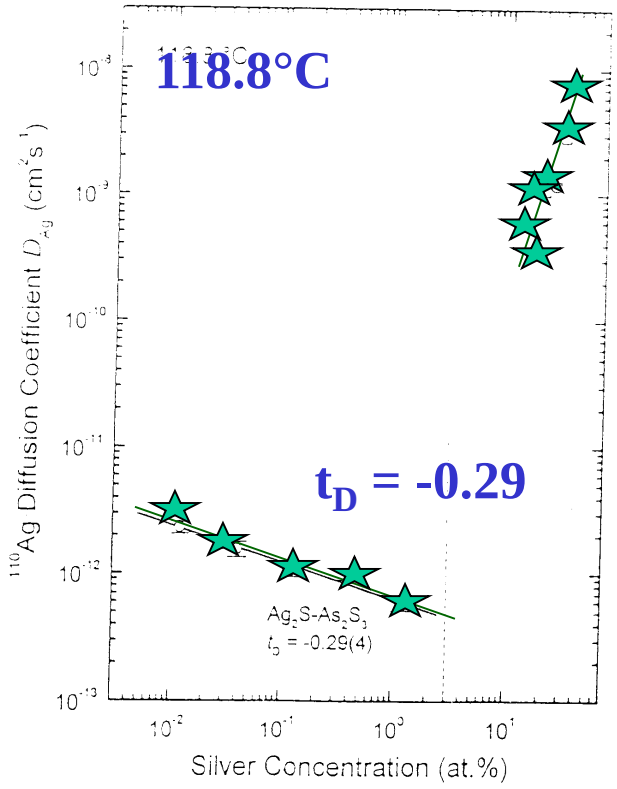
$Ag_2S - As_2S_3$ glasses

Conductivity



Log-log plots

^{110m}Ag tracer diffusion coefficient



$\sigma = C_\sigma x^{t\sigma}$ $t_D = t_\sigma - 1$

low silver content: conductivity mainly ionic $D = C_D x^{tD}$

high silver content: conductivity purely ionic $t\sigma > 0.99$

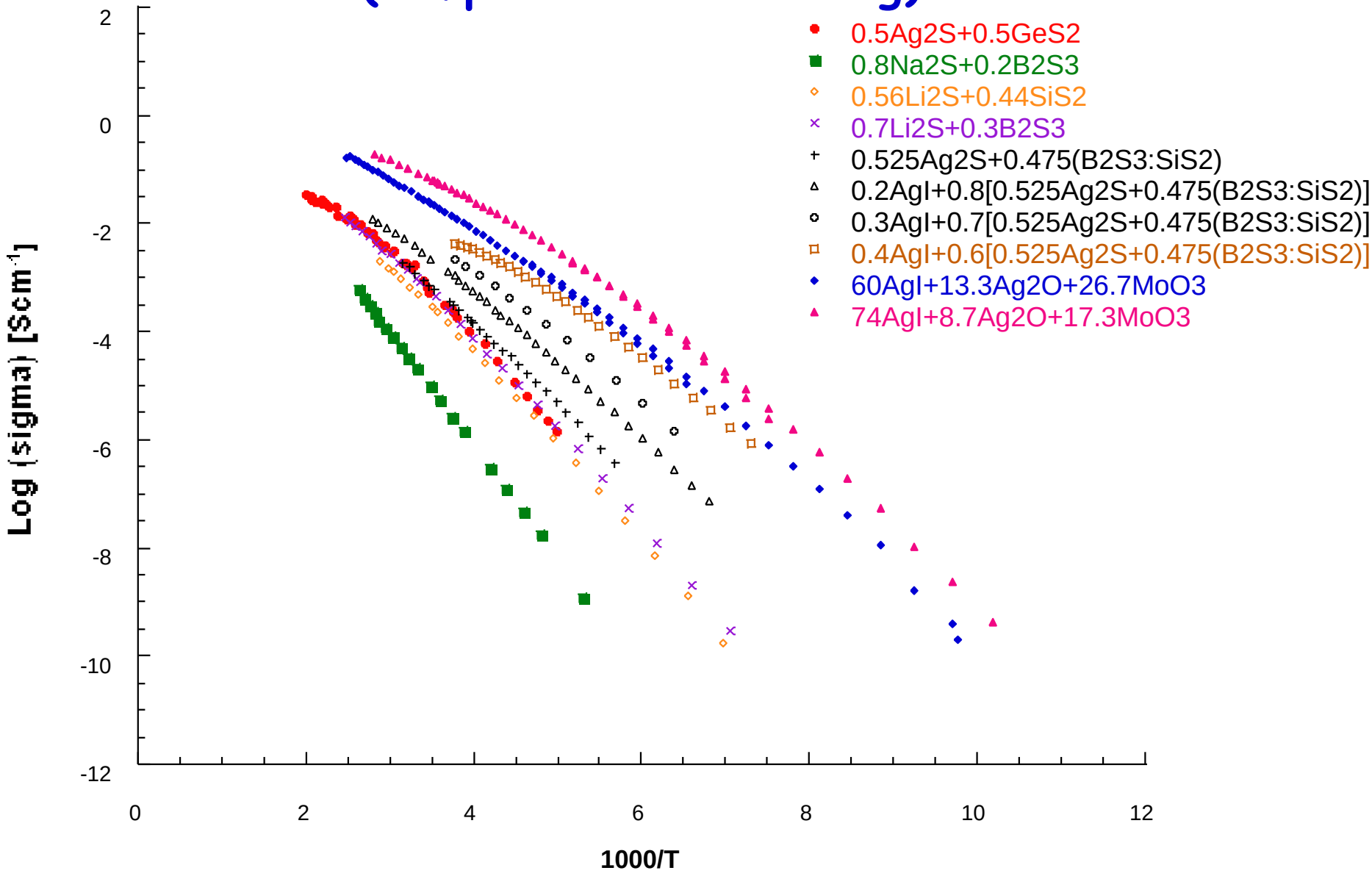
(same conclusions for: Ag2S-GeS2 and Ag2S-GeS-GeS2)

Bychkov E, Tsegelnik V, Vlasov Y, Pradel A and Ribes M., JNCS 208 (1996) 1.

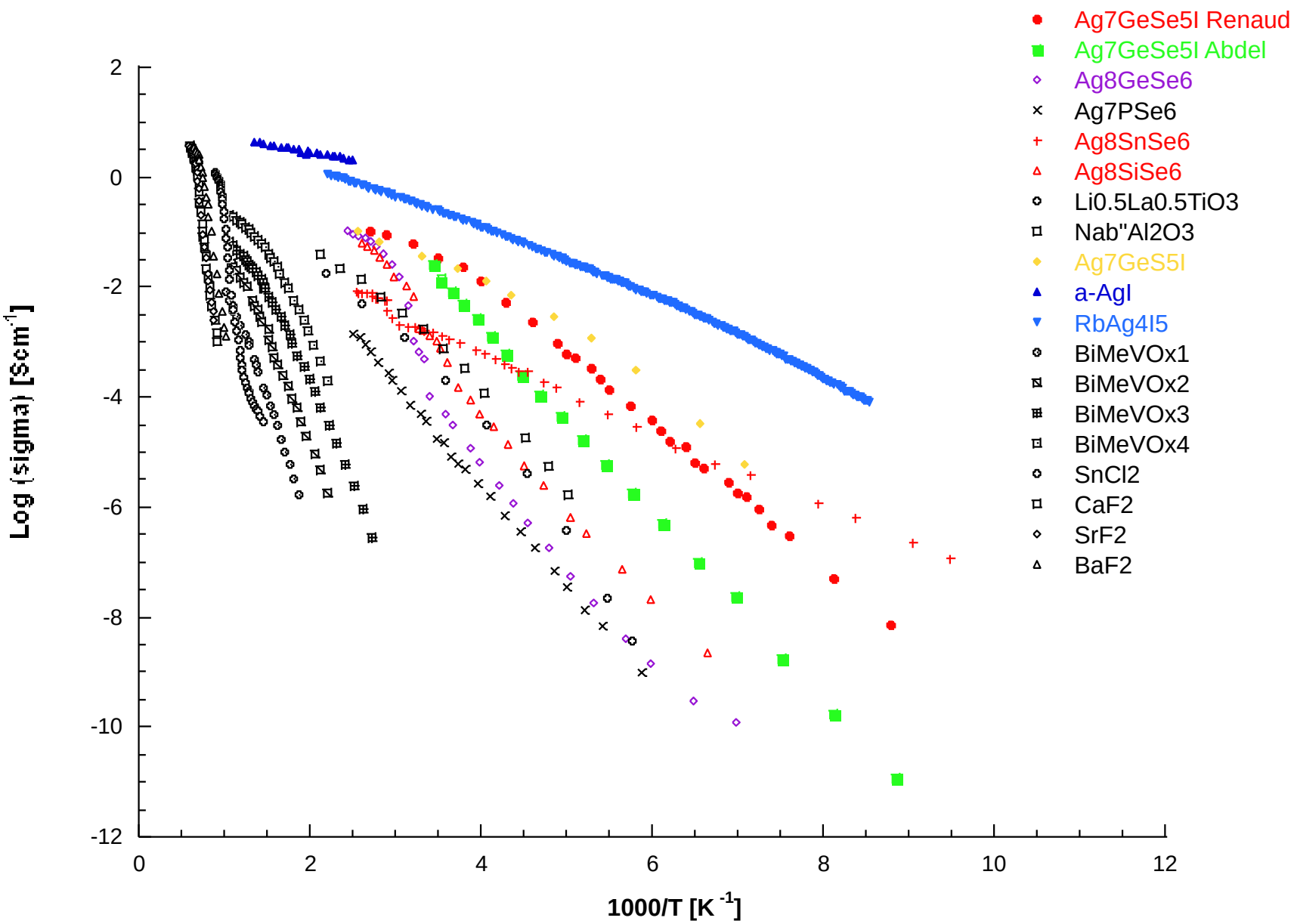
Bychkov E, Bychkov A, Pradel A and Ribes M., SSI 113-115 (1998) 691.

Non-Arrhenius behaviour ($\log \sigma \propto 1/T$) in glasses and more generally in super-ionic conductors

Arrhenius plots of σ for different « superionic » glasses (temperatures below Tg)



Arrhenius plots of σ for different « superionic » Crystallised phases



Because of super-Arrhenius behaviour below Tg in glasses one can think that it exists a « Mobile ion » glass transition

Such a transition cannot be observed easily because its weakness. (To date it has only been reported by Hahashi and Ojuni – AgPO3-AgI glass at ~80K).

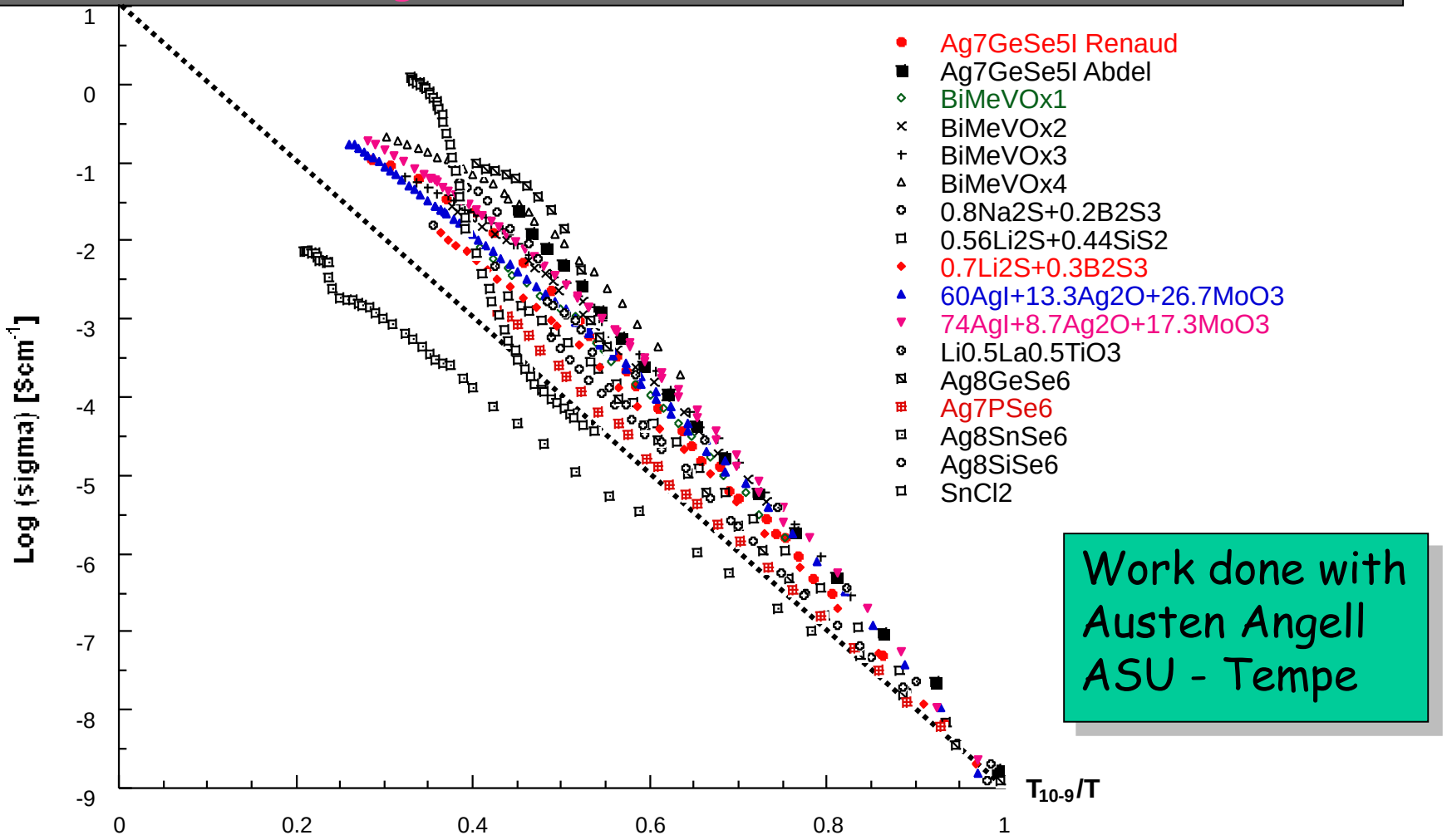
It is also possible to imagine a « mobile ion Tg »for superionic crystalline compounds with disorder in the mobile ion sub-lattice (for temperature higher than this hypothetical temperature ions move in a quasi-liquid sub-lattice)

F

For temperature greater than that of « mobile ion Tg » cooperative cation motions ⟶ super-Arrhenius behaviour

Scaled Arrhenius plots of σ for different « superionic » Glass and Crystalline compounds

In the absence of experimental data one can tentatively take for « mobile ion Tg » the temperature where the conductivity is about 10^{-9} Scm-1, allowing a scaling of the variation of the conductivity ($\log \sigma \propto T(\sigma = 10^{-9}) / T$)



Work done with
Austen Angell
ASU - Tempe

STOP pour le moment