Conductivité ionique dans les verres

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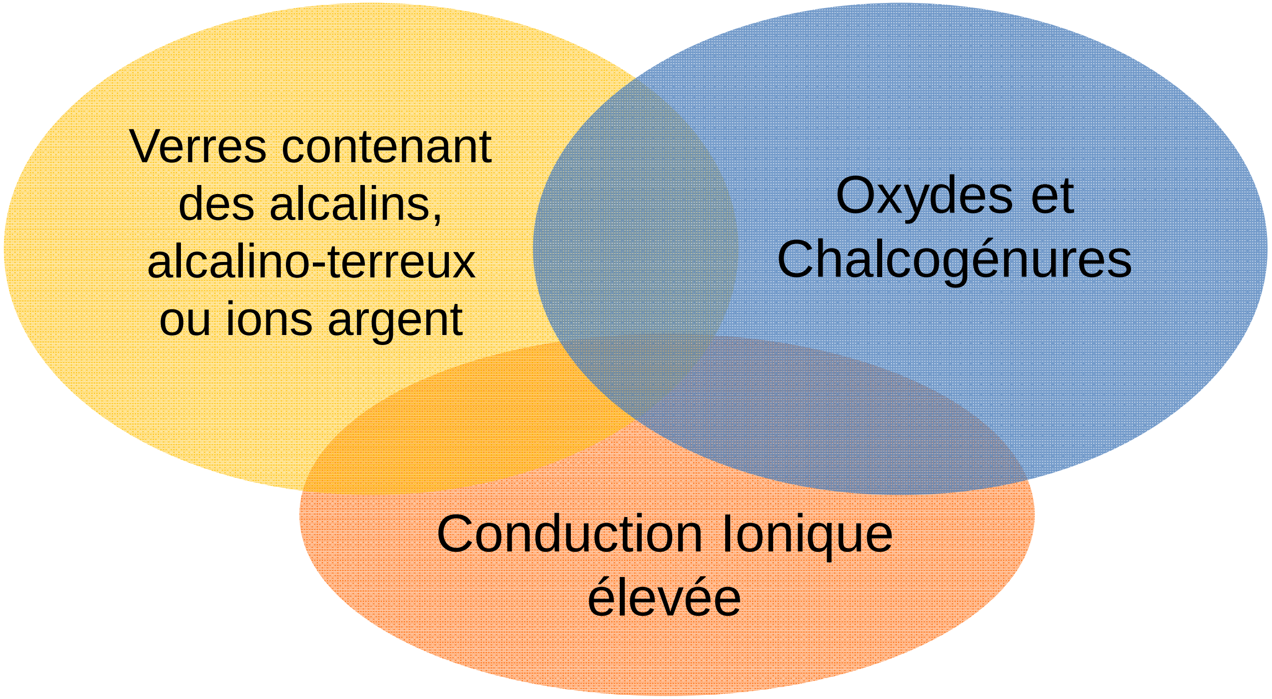


Dispositifs de stockage de lœnergie

Batteries tout-solide

Dispositifs de stockage de lôinformation

Mémoires ioniques

Spectroscopie d'impédance Complexe

Une succession de signaux de **tension sinusoïdale U(ω)** de fréquences différentes est appliquée à lœchantillon

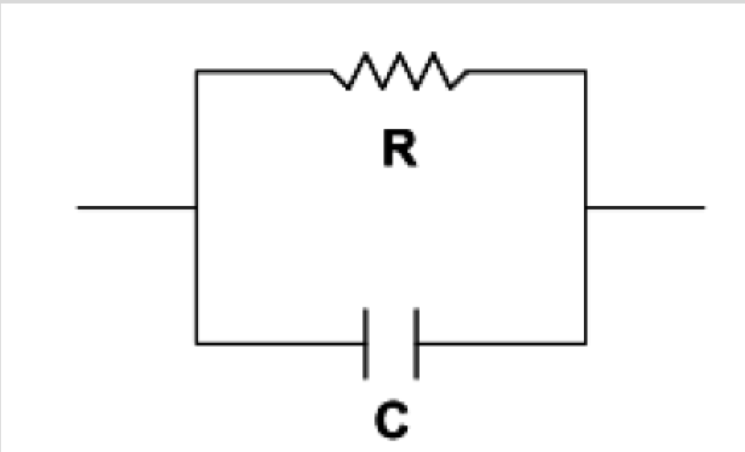
e = épaisseur de lœchantillon,
S = surface métallisée en contact avec lœlectrode

Intensité sinusoïdale I(ω) enregistrée

Impédance du matériau

$$Z(\omega) = \frac{U(\omega)}{I(\omega)} = \frac{U^0 \exp(j\omega t)}{I^0 \exp(j\omega t + \varphi)} = |Z| \exp(-j\varphi)$$

Circuit modélisant le comportement électrique dœun verre



$$Z = \frac{R}{1 + j\tau\omega} = \mathrm{Re}(Z) + j\,\mathrm{Im}(Z)$$

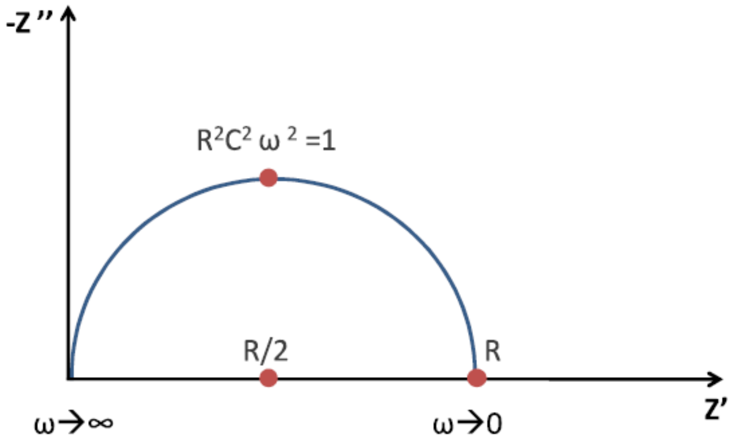
$$\mathrm{Re}(Z) = \frac{R}{1 + \tau^2\omega^2}$$

$$\mathrm{Im}(Z) = \frac{-R\tau\omega}{1 + \tau^2\omega^2}$$

avec τ = RC (constante de temps)

Spectroscopie d'impédance Complexe

Diagramme de Nyquist



R= résistance

Conductivité

$$\sigma = \frac{1}{R} \times \frac{e}{S}$$

e = épaisseur de lœchantillon,
S = surface métallisée en contact avec lœlectrode

Dépendance avec la température : Loi dôArrhenius

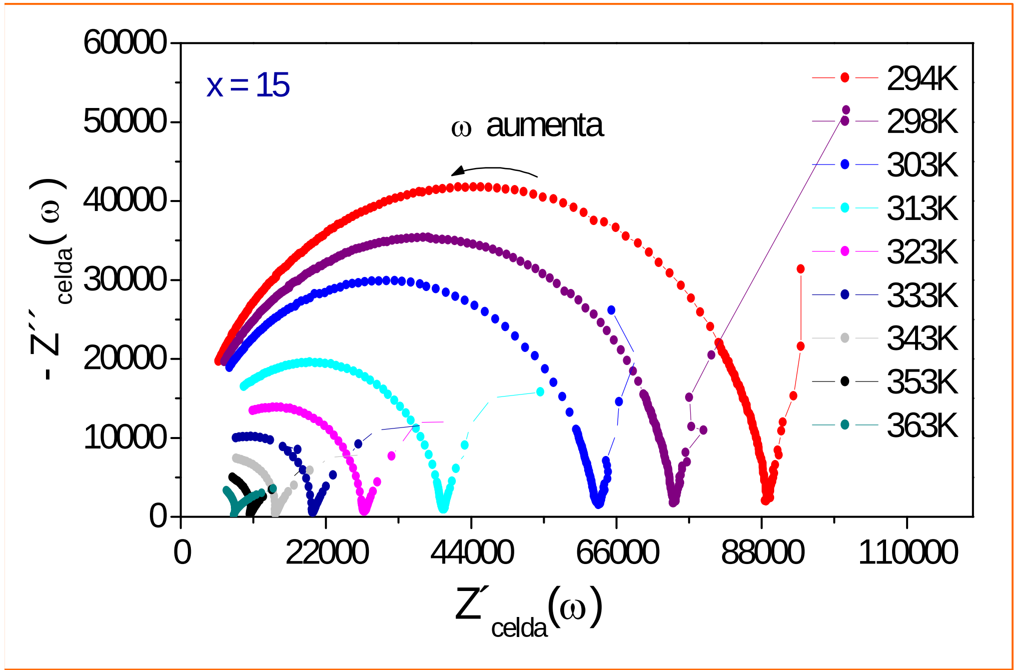
$$\sigma = \frac{\sigma_0}{T}\exp(-E_\sigma / kT)$$

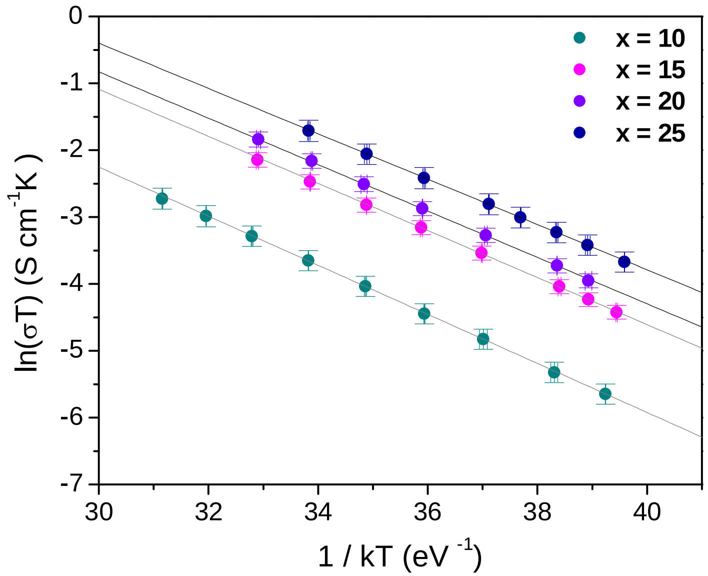
$$ln(\sigma.T) = -\frac{E_\sigma}{kT} + ln\,\sigma_0$$

E_σ : énergie dâctivation
σ_0: terme pré-exponentiel

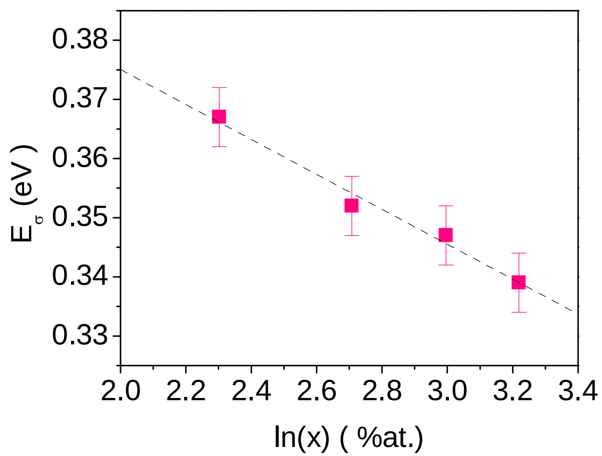
Lœnergie dâctivation est déterminée en calculant, par régression linéaire, la pente de la droite ln(σT) = f(1/kT).

Spectroscopie d'impédance Complexe : Système $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$

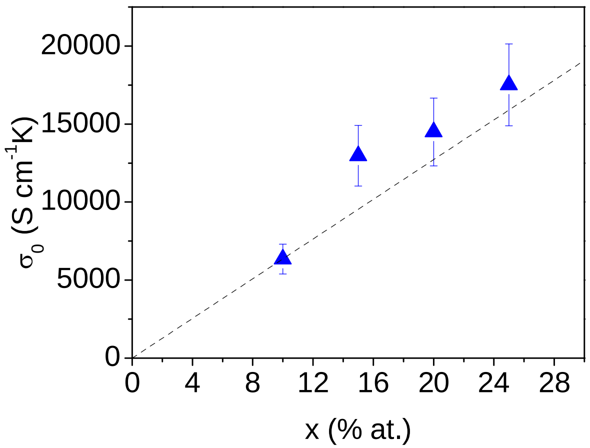




Energie dâctivation



Terme pré-exponentiel



M. A. Ureña, A. A Piarristeguy. M. Fontana, B. Arcondo; SSI 176 (2005) 505.

A. Piarristeguy, J. M. Conde Garrido, M. A. Ureña, M. Fontana, B. Arcondo; J. Non-Cryst.Sol. 353 (2007) 3314.

Ion conducting glasses

Mixed glass former effect: Oxide glasses

System : $45\ Li_2O$ ï $55\ [x\ B_2O_3$ ï $(1-x)\ P_2O_5)]$

(structure locale, ^{11}B RMN, ^{31}P RMN)

Mixed glass former effect: Chalcogenide glasses

Systems : $0.3\ Li_2S\ 0.7[(1-x)SiS_2\ xGeS_2]$, $0.5\ Li_2S\ 0.5[(1-x)SiS_2\ xGeS_2]$

(structure locale, SAXS, Tg)

Ag-based glasses

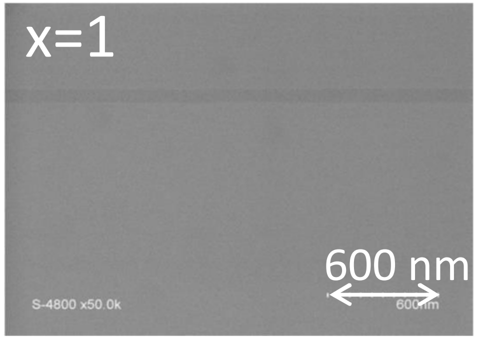
Systems : $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$, Ag_2S-GeS_2, Ag_2S-GeS-GeS_2, Ag_2S-As_2S_3

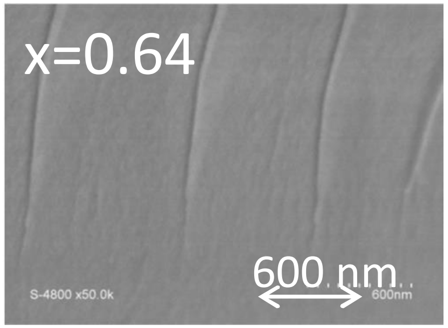
(separation de phases, EFM, C-AFM)

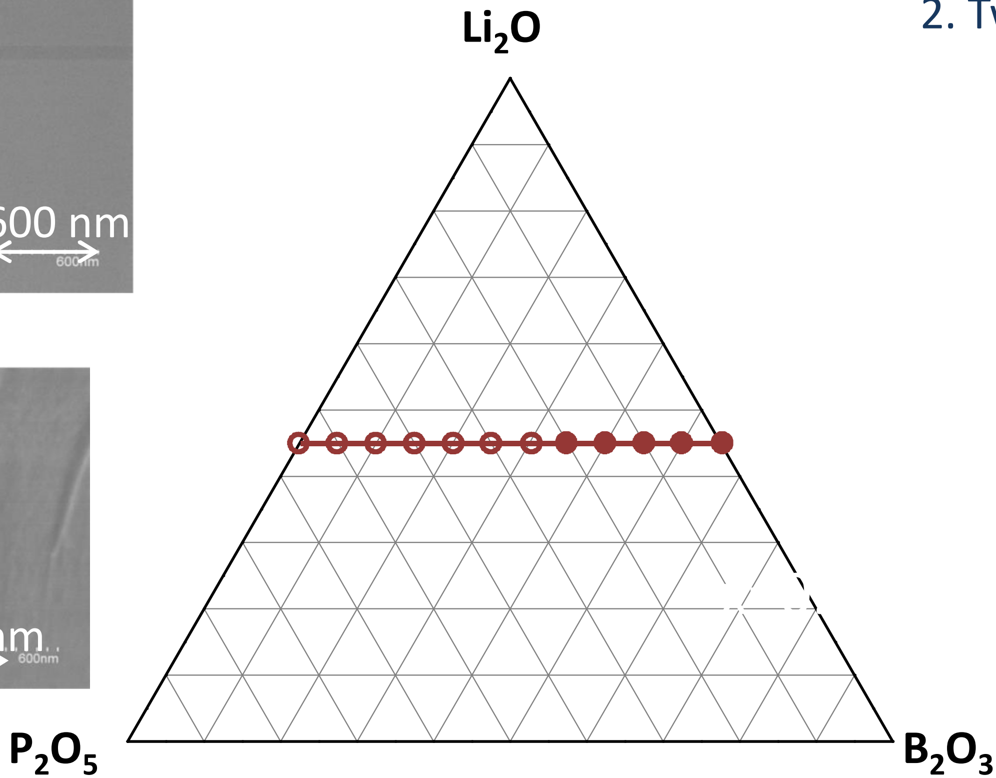
Mixed glass former effect: Oxide glasses

Thèse B. Raguenet

System : $45\ Li_2O - 55\ [x\ B_2O_3 - (1\text{-}x)\ P_2O_5)]$







Extension of vitreous domain up to x=1

2. Twin roller quenching

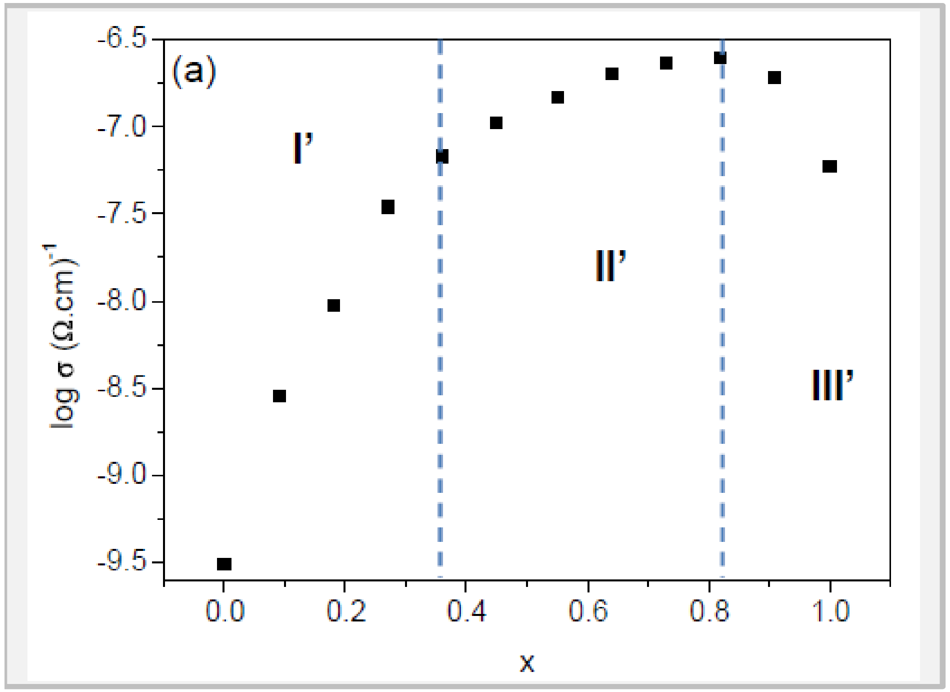
B. Raguenet, G. Tricot, G. Silly, M. Ribes and A. Pradel, Solid State Ionics, 208, 2012, 25-30

System 45 Li_2O ï 55 [x B_2O_3 ï (1-x) P_2O_5)]: conductivity

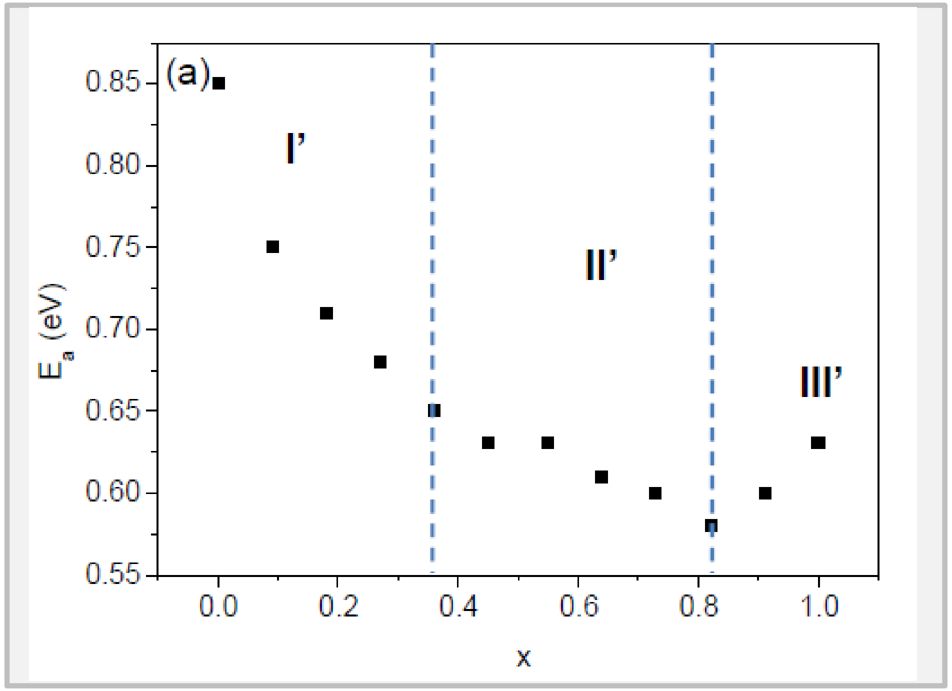
Mixed glass former effect: Oxyde glasses

System : 45 Li_2O – 55 [x B_2O_3 – (1-x) P_2O_5)]

Conductivity



Activation energy



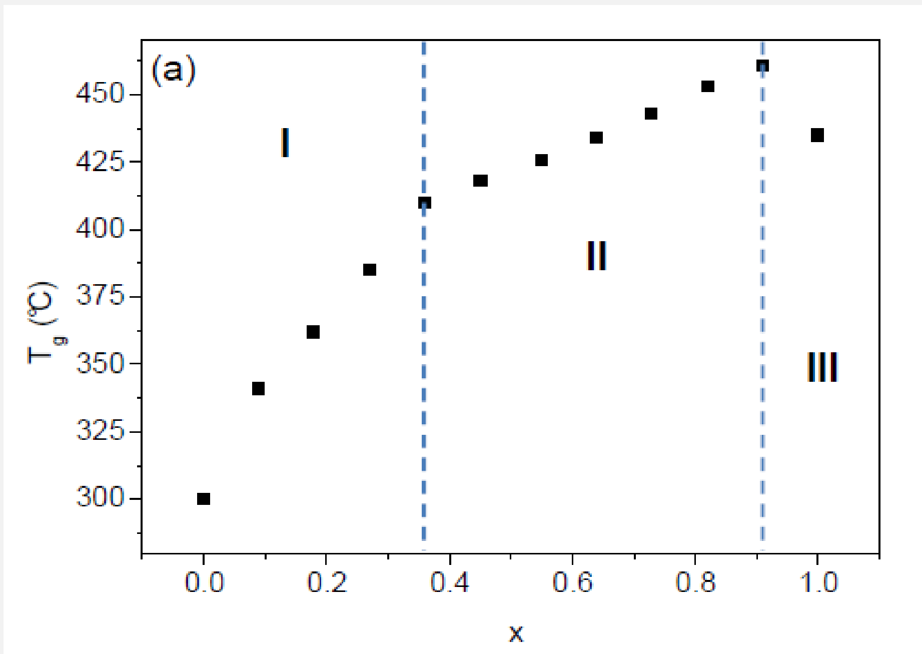
B. Raguenet, G. Tricot, G. Silly, M. Ribes and A. Pradel, Solid State Ionics, 208, 2012, 25-30

System 45 Li_2O ï 55 [x B_2O_3 ï (1-x) P_2O_5)]: Tg

Mixed glass former effect: Oxyde glasses

System : 45 Li_2O – 55 [x B_2O_3 – (1-x) P_2O_5)]

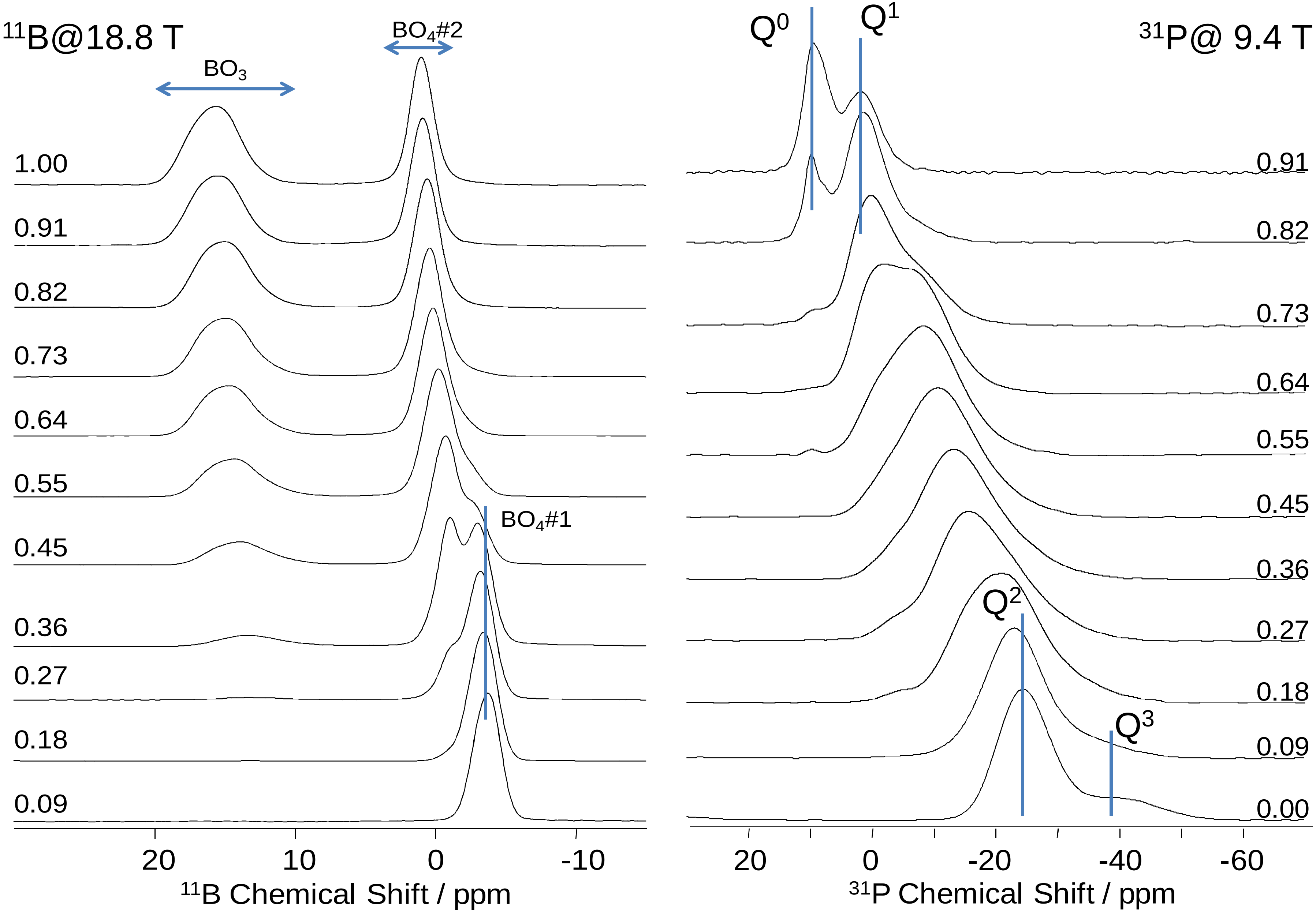
Glass transition temperature



B. Raguenet, G. Tricot, G. Silly, M. Ribes and A. Pradel, Solid State Ionics, 208, 2012, 25-30

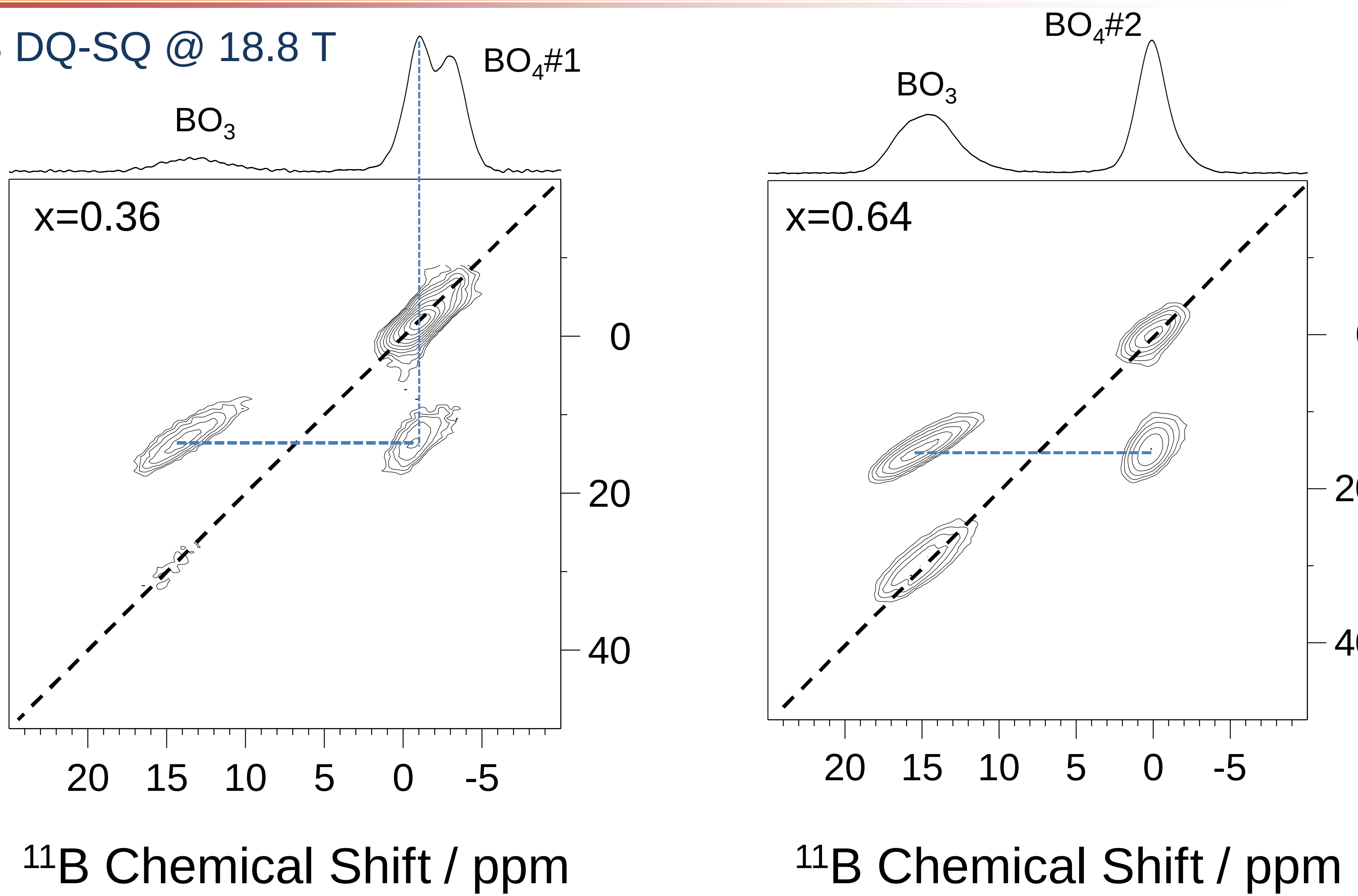
System 45 Li_2O ï 55 [x B_2O_3 ï (1-x) P_2O_5)]: RMN

G. Tricot
TGIR Lille



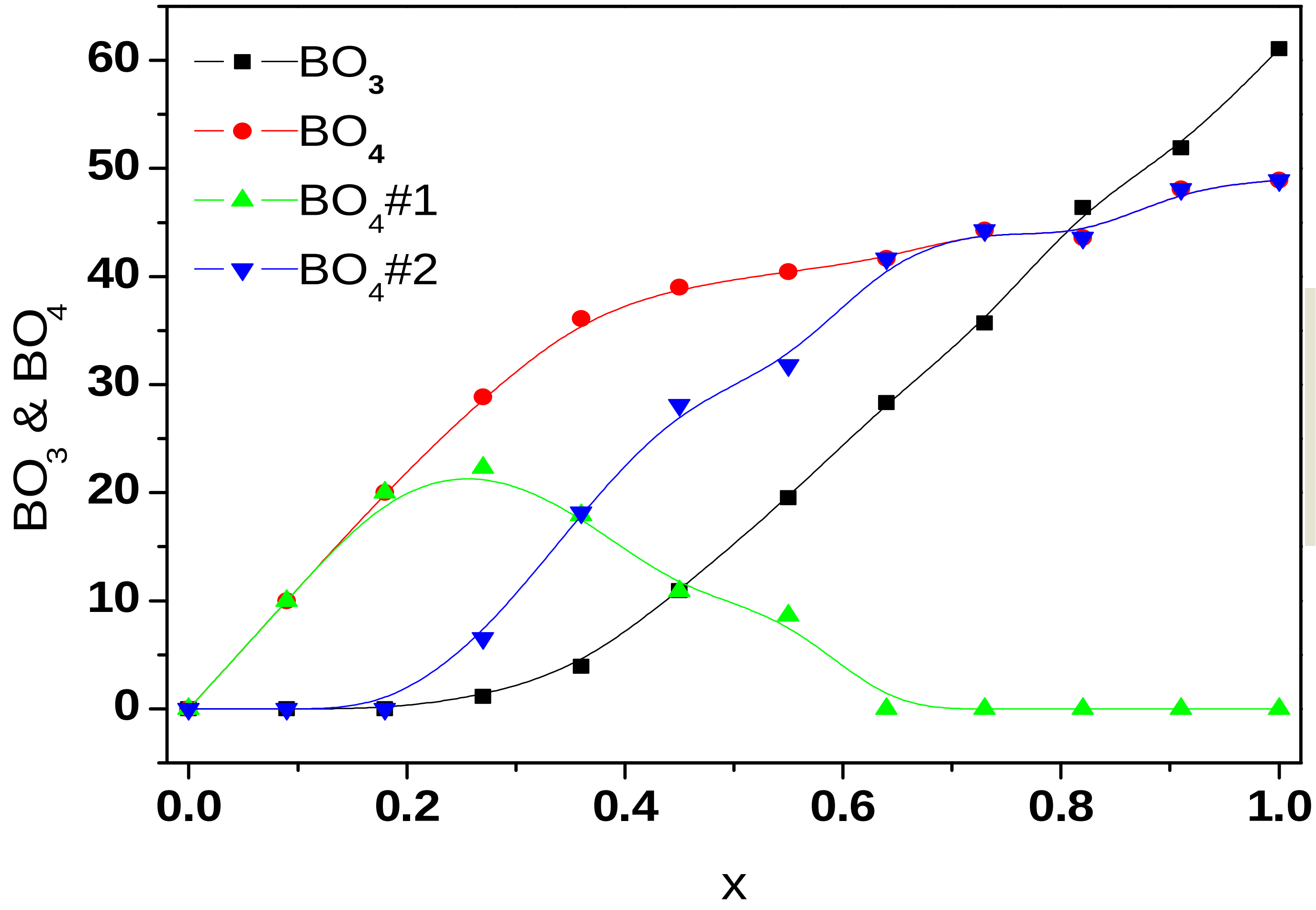
System 45 Li_2O ï 55 [x B_2O_3 ï (1-x) P_2O_5)]: RMN

^{11}B DQ-SQ @ 18.8 T



B. Raguenet, G. Tricot, G. Silly, M. Ribes and A. Pradel, J. Mat. Chem. 21, 2011, 17693

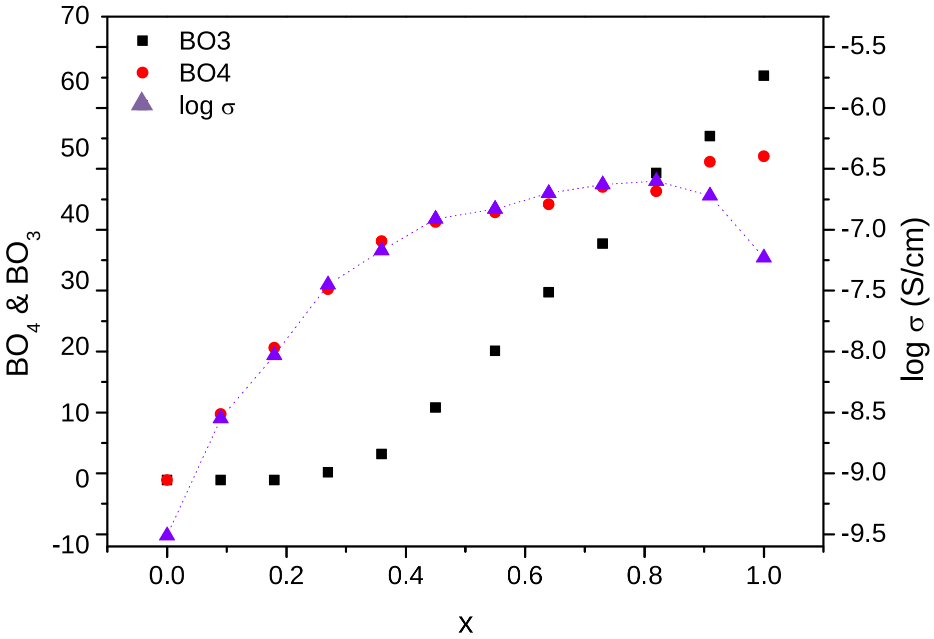
System 45 Li_2O ï 55 [x B_2O_3 ï (1-x) P_2O_5)]: RMN



B. Raguenet, G. Tricot, G. Silly, M. Ribes and A. Pradel, J. Mat. Chem. 21, 2011, 17693

System 45 Li_2O ï 55 [x B_2O_3 ï (1-x) P_2O_5)]: RMN

✓ The *Mixed Network Former Effect* is directly related to the BO_4 units!



- The coordination alone impacts the conductivity!
  Li^+ acts as a charge compensator in the presence of BO_4 units. It is then more mobile than Li^+ close to non bridging oxygen

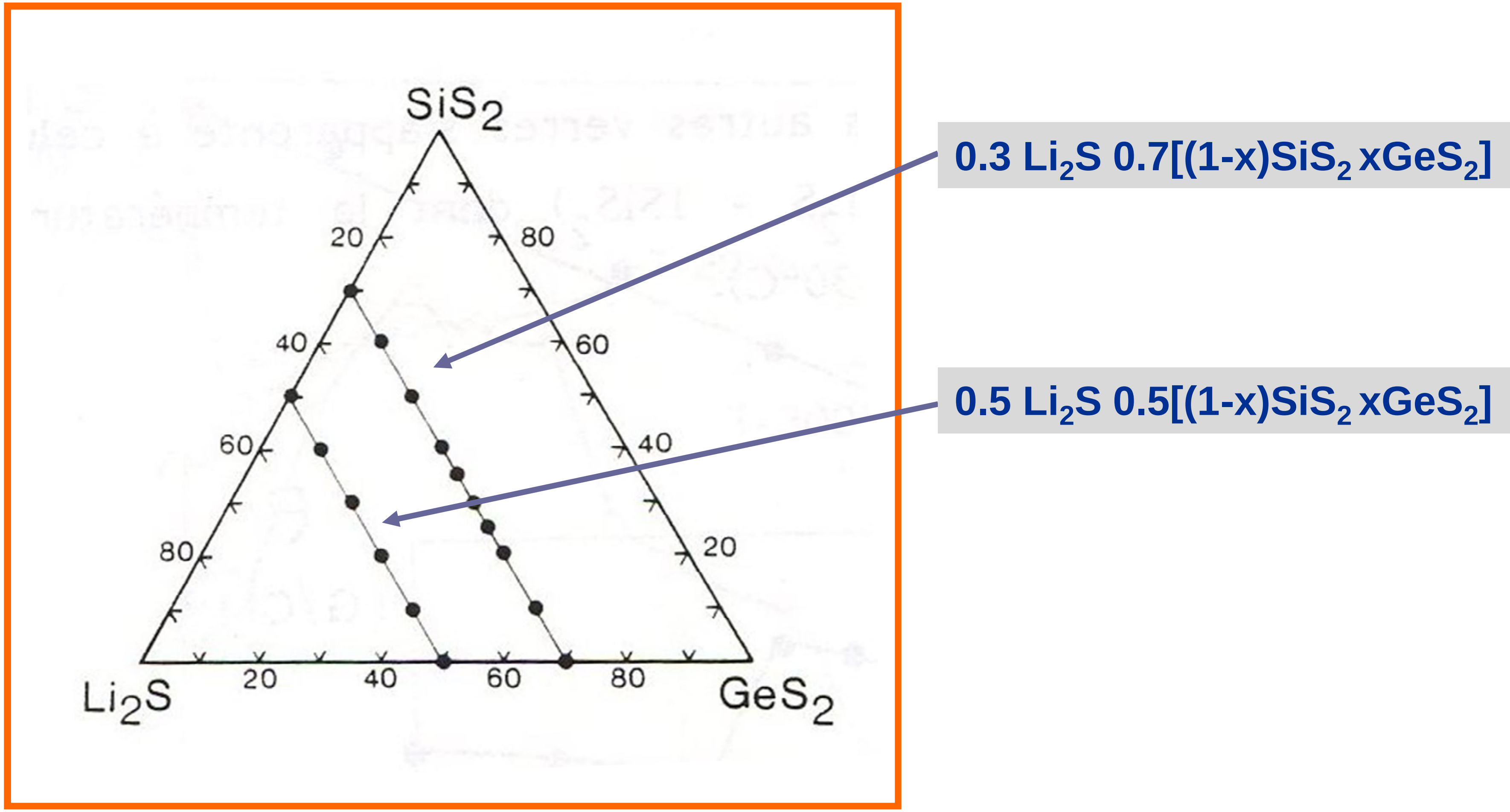
- The presence of phosphorous helps essentially in favouring the existence of BO_4 against BO_3

- The decrease in conductivity at high boron content occurs when the ratio $BO_3/BO_4>1$. BO_3 units probably break the conduction paths.

B. Raguenet, G. Tricot, G. Silly, M. Ribes and A. Pradel, J. Mat. Chem. 21, 2011, 17693

System Li_2S- [(1-x)SiS_2-xGeS_2]

Mixed glass former effect: Chalcogenide glasses

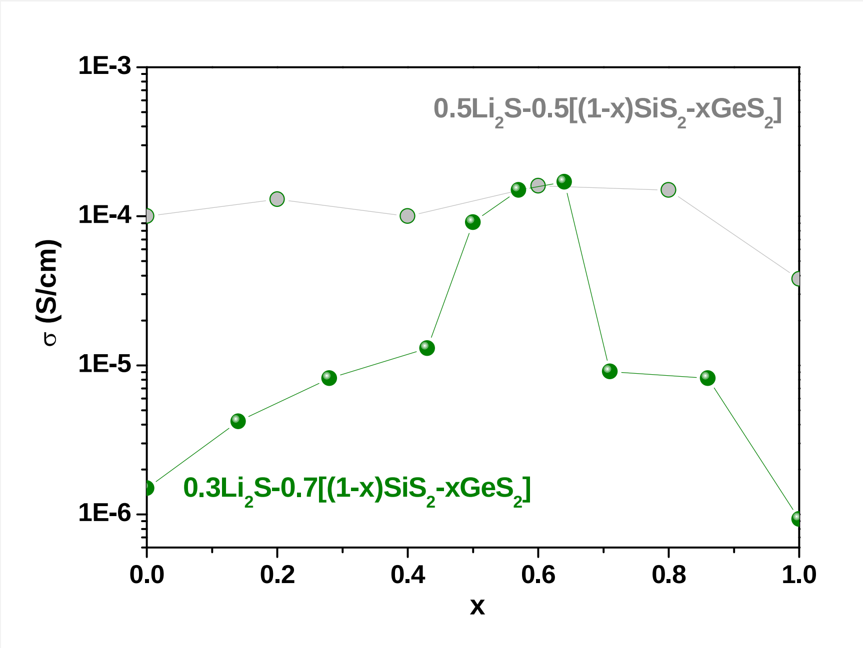


V.K. Deshpande, A. Pradel, M. Ribes, Mat. Research Bull., 23(3), 379 (1988)

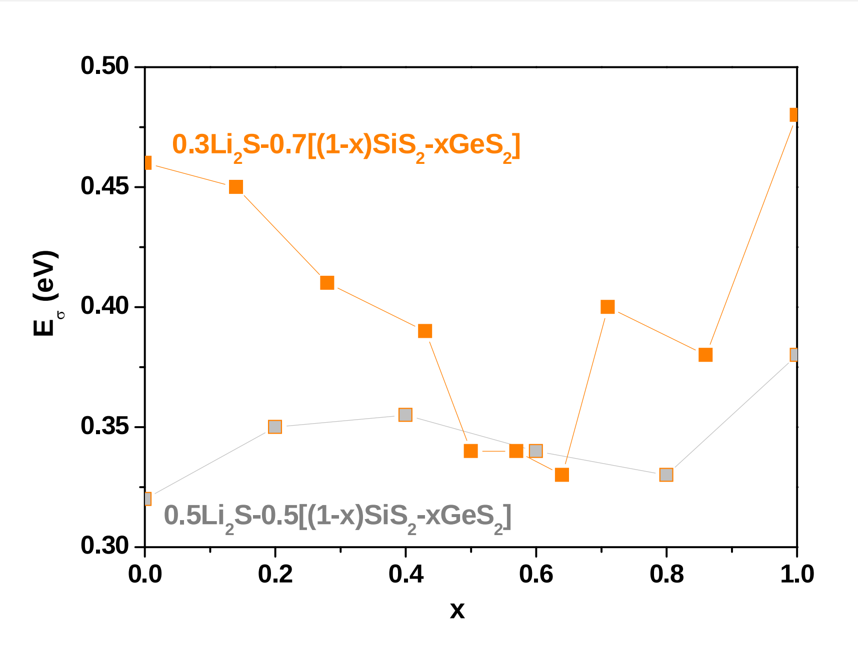
System Li_2S- [(1-x)SiS_2-xGeS_2]:: Conductivity and E_σ

Mixed glass former effect: Chalcogenide glasses

Conductivity



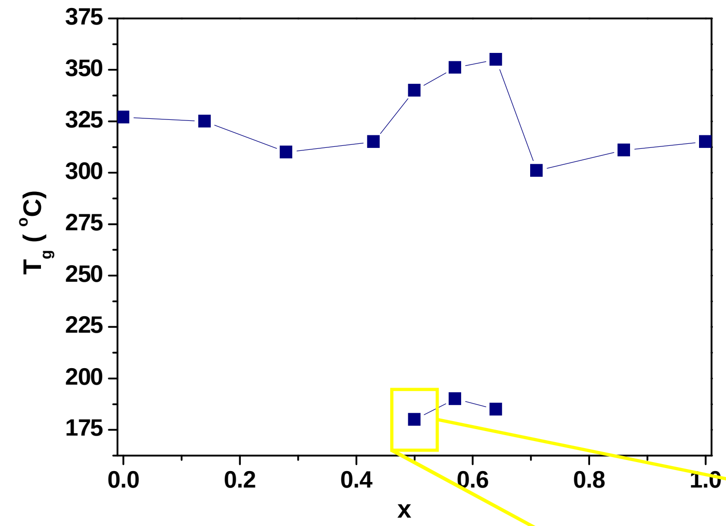
Activation energy



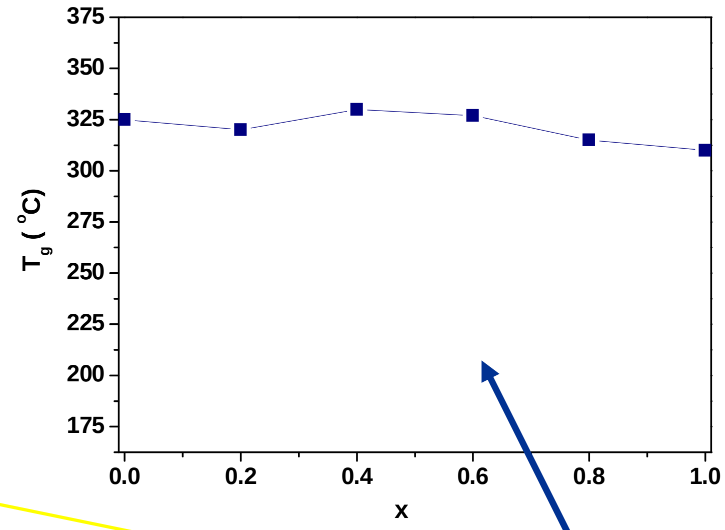
V.K. Deshpande, A. Pradel, M. Ribes, Mat. Research Bull., 23(3), 379 (1988)

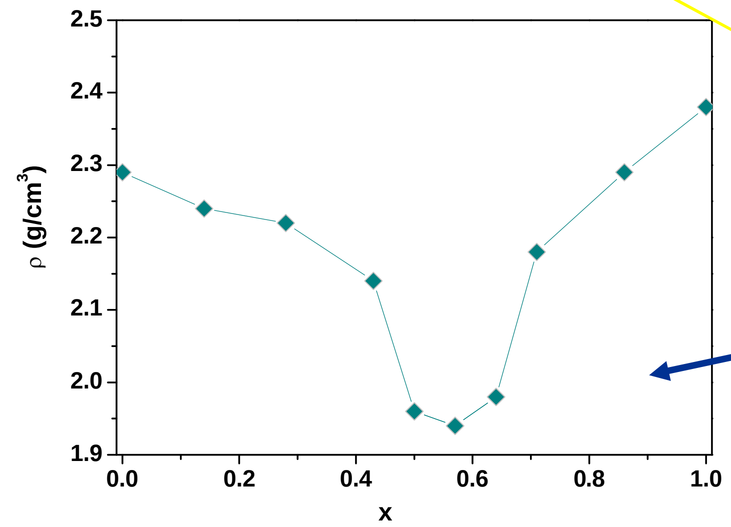
System Li_2S- [(1-x)SiS_2-xGeS_2]: Tg and density

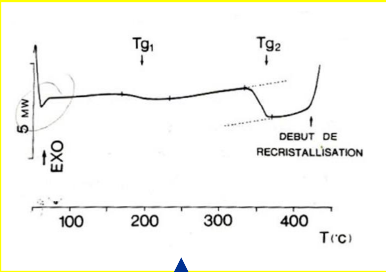
0.3 Li_2S 0.7[(1-x)SiS_2 xGeS_2]



0.5 Li_2S 0.5[(1-x)SiS_2 xGeS_2]





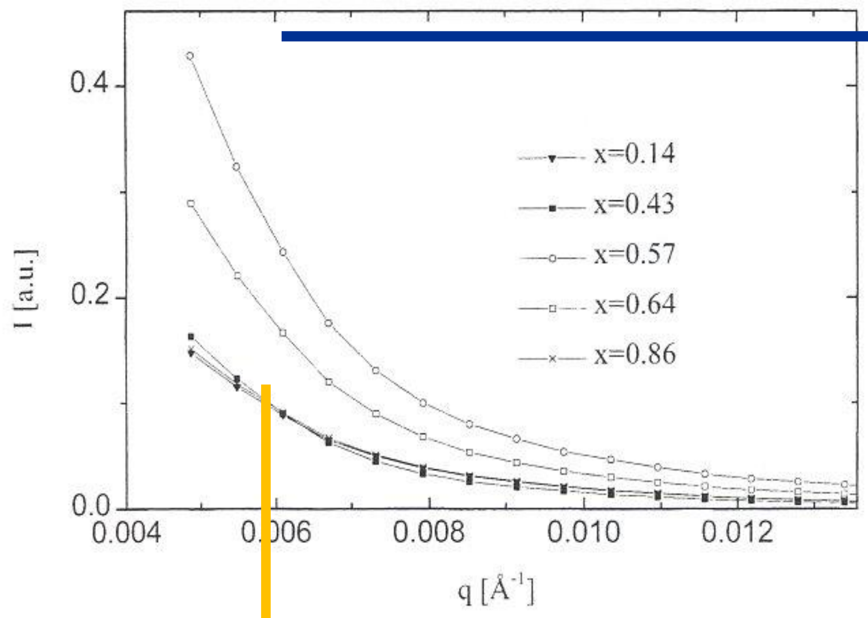


Smooth change in T_g

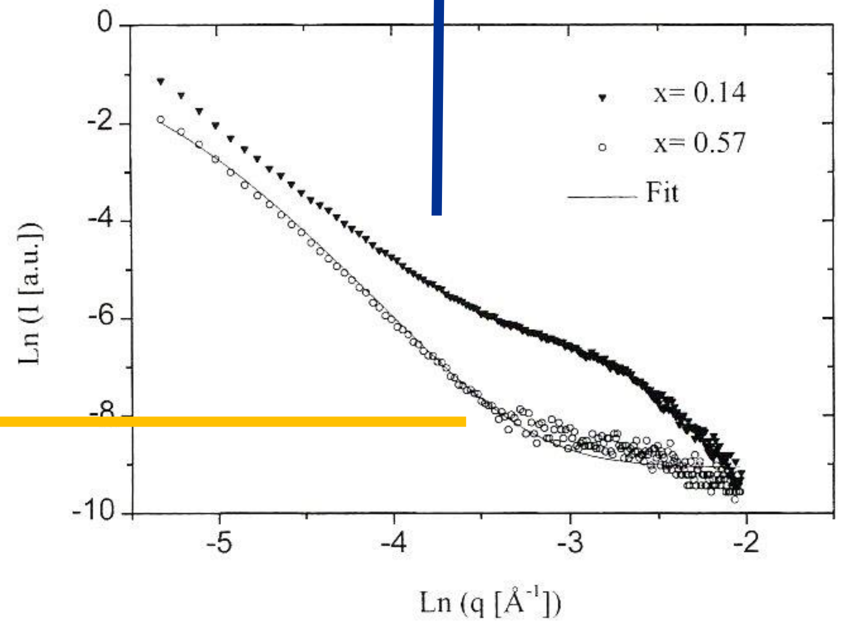
2 T_g and a minimum in ρ for ~50:50 ratio in former content

System Li_2S- [(1-x)SiS_2-xGeS_2]: SAXS

0.3 Li_2S 0.7[(1-x)SiS_2 xGeS_2]



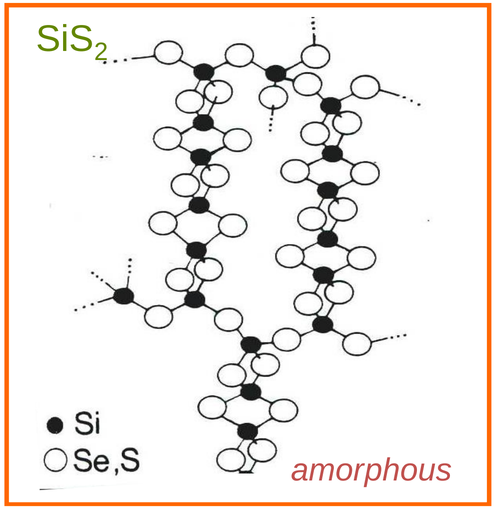
Porod Law:
aggregates or clusters of 50 Å in size



Debye-Bueche model:
homogeneous glasses

A. Pradel, Ch. Rau, D. Bittencourt, P. Armand, E. Philippot, M. Ribes Chemistry of Materials, 10 (8), 2162-2166 (1998).

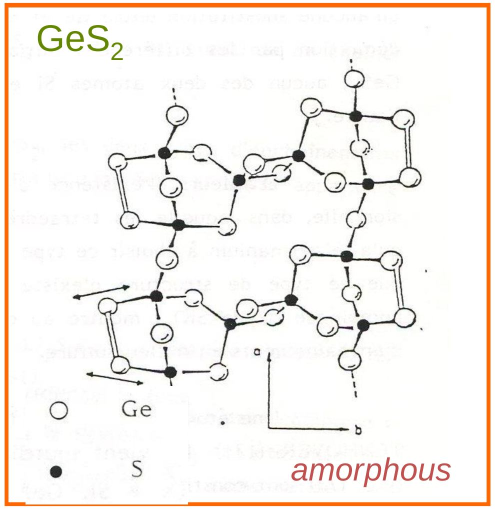
System Li_2S- [(1-x)SiS_2-xGeS_2]: Structure



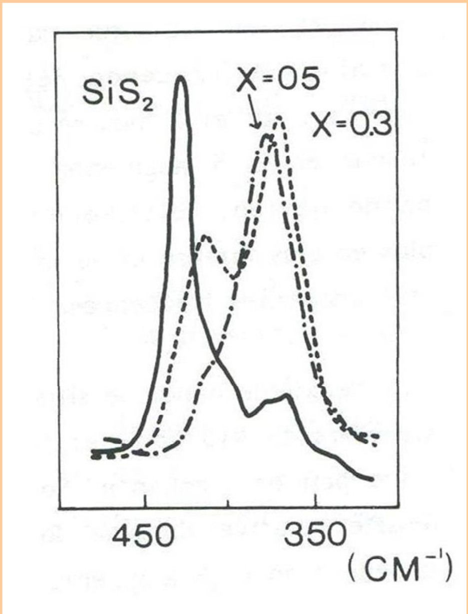
Different medium range order

No possible mixing of the two formers

Complete phase Separation (Tenhover 1983)



xLi_2S- (1-x)SiS_2



Addition of Li_2S

Preferential destruction of edge sharing tetrahedra (^{29}Si NMR investigation)

x=0.3 different MRO

phase separation

x=0.5 similar MRO

Complete solid solution

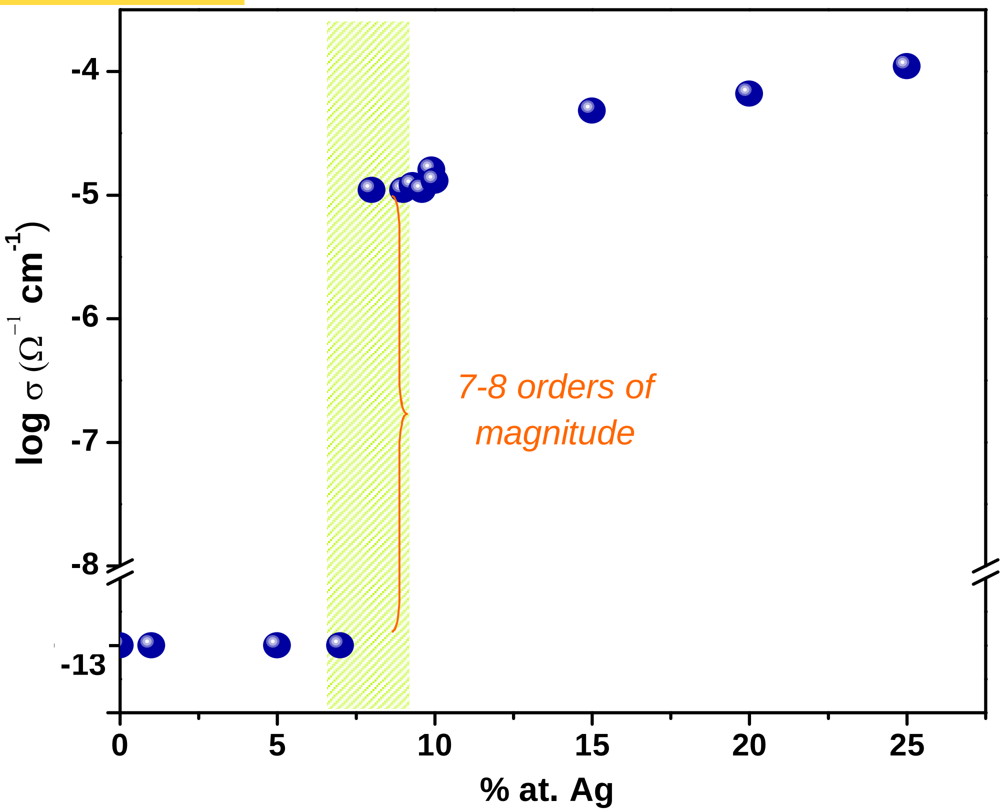
A. Pradel, Ch. Rau, D. Bittencourt, P. Armand, E. Philippot, M. Ribes
Chemistry of Materials, 10 (8), 2162-2166 (1998).

Structure / Electrical properties: Ag-Ge-Se(S) systems

Samples

$Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ with **0 < x < 30 % at.**

Conductivity



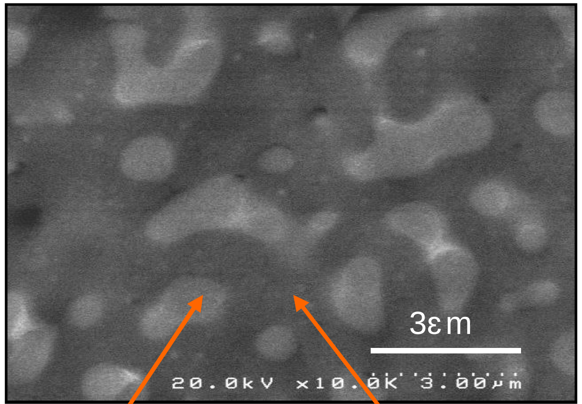
A sudden break in the « conductivity vs Ag content » curve for 8-10% in Ag

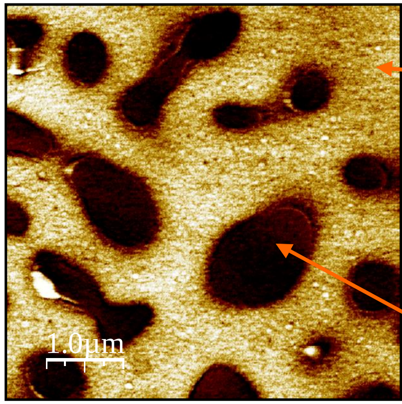
M. A. Ureña, A. A Piarristeguy. M. Fontana, B. Arcondo; SSI 176 (2005) 505.
A. Piarristeguy, J. M. Conde Garrido, M. A. Ureña, M. Fontana, B. Arcondo; J. Non-Cryst.Sol. 353 (2007) 3314.

Microstructural study : $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ glasses

FE-SEM | **EFM V = - 5V**

Ag5





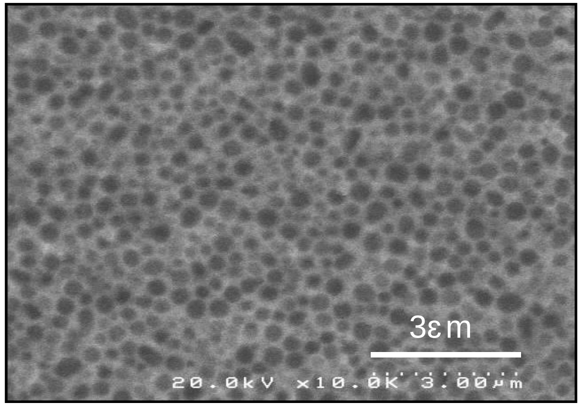
Clear-areas (Ag-poor phase)

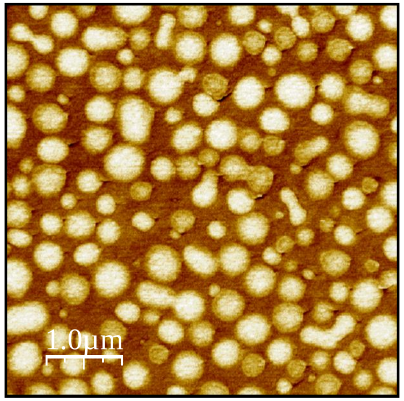
Dark-areas (Ag-rich phase)

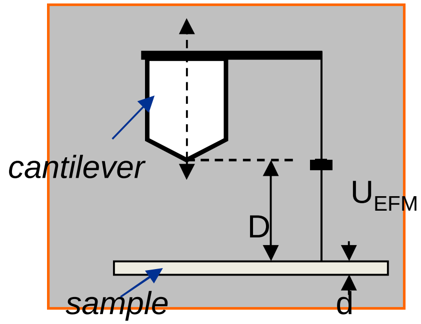
Clear-areas (Ag-rich phase)

Dark-areas (Ag-poor phase)

Ag15



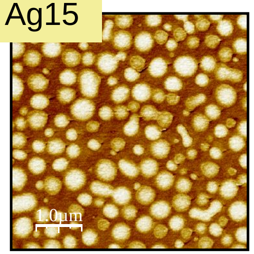




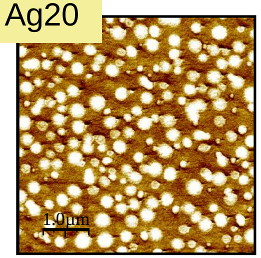
A.A. Piarristeguy, M. Ramonda, M.A. Ureña, A. Pradel, M. Ribes, J. Non-Cryst. Solids 353 (2007) 1261-1263.

Microstructural study : $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ glasses

Ag15

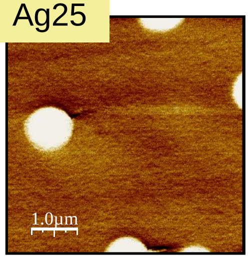


Ag20

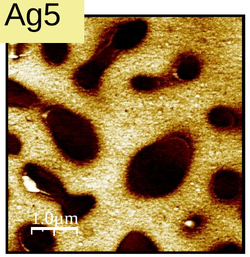


Ag-rich phase
embedded in
Ag-poor phase

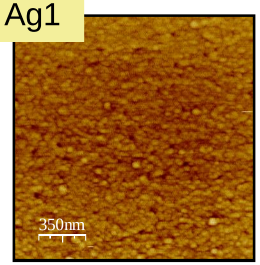
Ag25

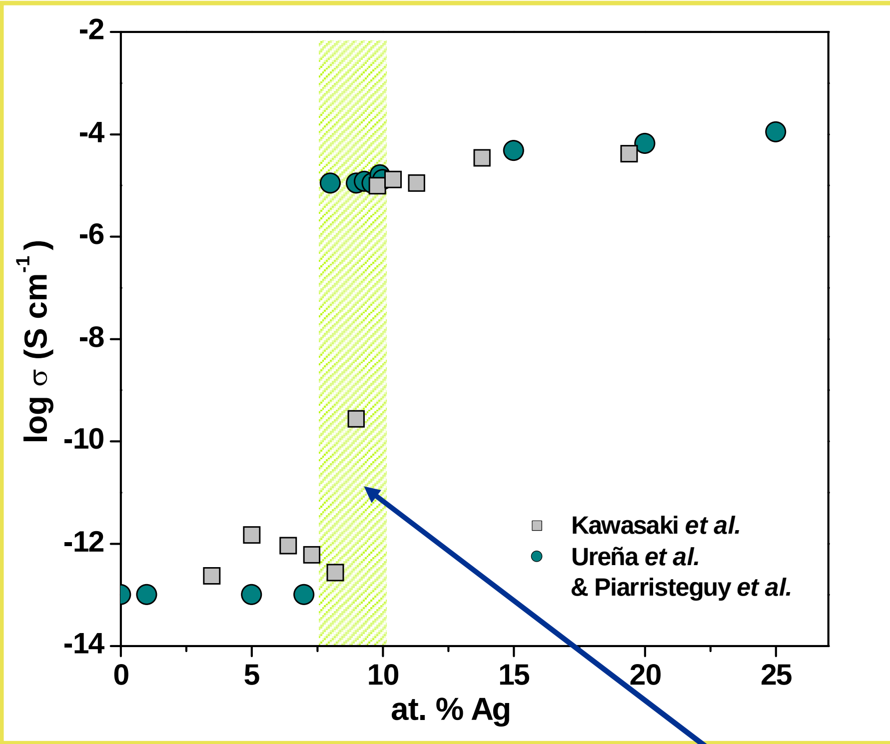


Ag5



Ag1



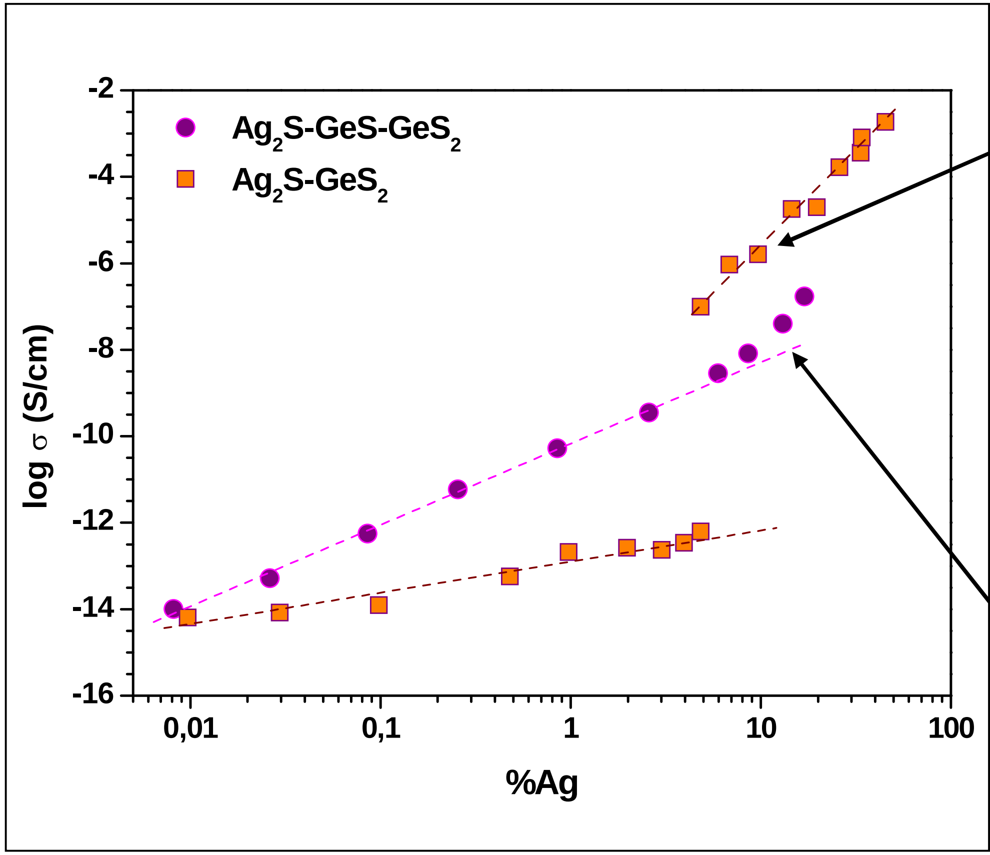


Ag-rich phase
is the **connecting**
phase

Percolation threshold

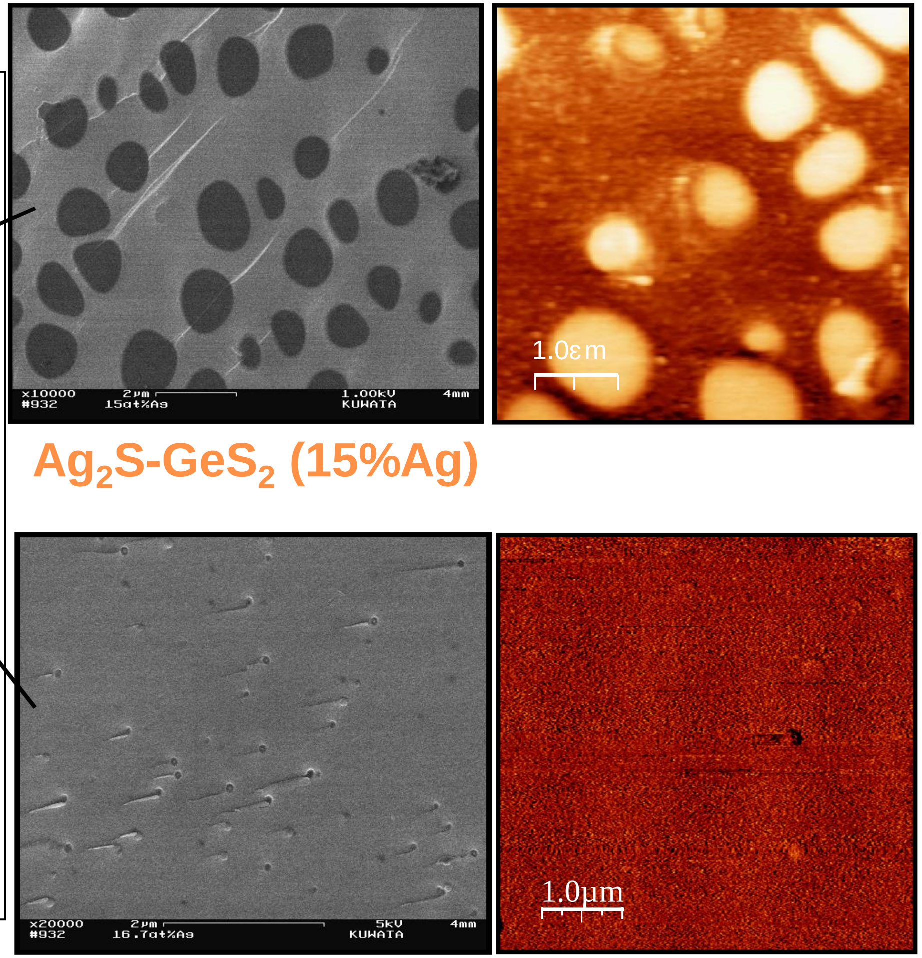
V. Balan, A.A. Piarristeguy, M. Ramonda, A. Pradel, M. Ribes, J. Optoelect. and Adv. Material Vol.8 ISS.6 (2006) 2112-2116.

Microstructural study : Ag-Ge-S glasses



E. Bychkov, V. Tsegelnik, Yu. Vlasov, A. Pradel, M. Ribes, J. Non-Cryst. Solids 208, 1 (1996).
A. Pradel, N. Kuwata, M. Ribes, J. Phys.: Condens. Matter 15, 1561 (2003).

FE-SEM **EFM -3V**



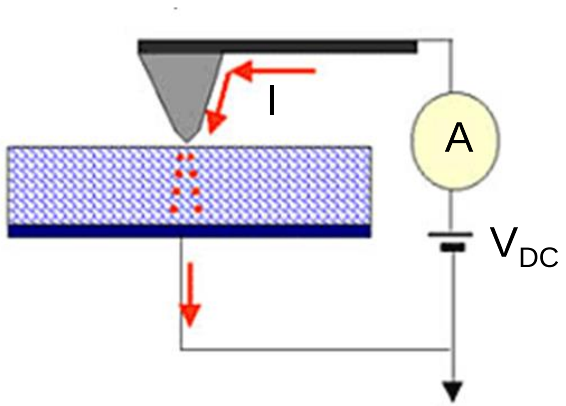
Ag_2S-GeS_2 (15%Ag)

Ag_2S-GeS-GeS_2 (16,7%Ag)

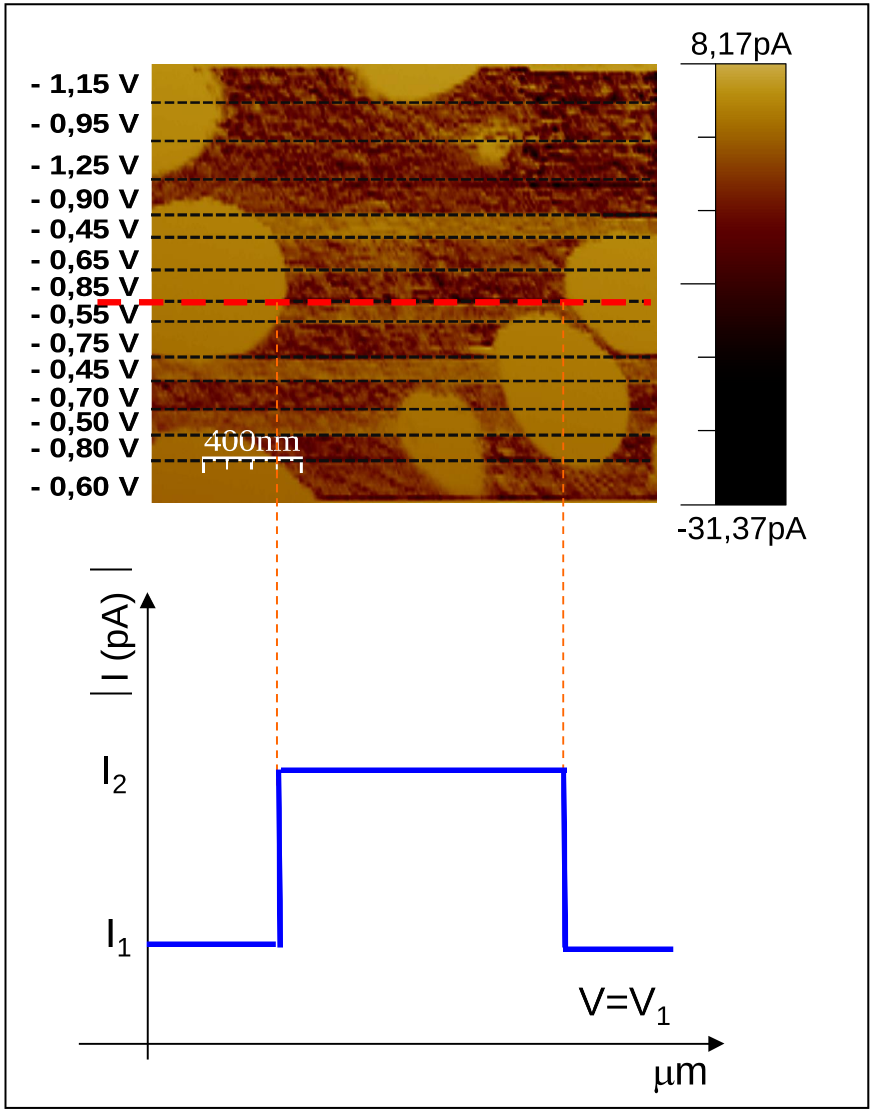
V. Balan, A.A. Piarristeguy, M. Ramonda, A. Pradel, M. Ribes, J. Optoelect. and Adv. Material Vol.8 ISS.6 (2006) 2112-2116.

Conductivity of each phase: Conductive Atomic Force Microscopy

✓ **C-AFM**



$Ag_{20}(Ge_{0.25}Se_{0.75})_{80}$



✓ The current through the **Ag-rich phase** increases when the applied dc bias increases.

✓ Practically any current flows through the **Ag-poor phase**.

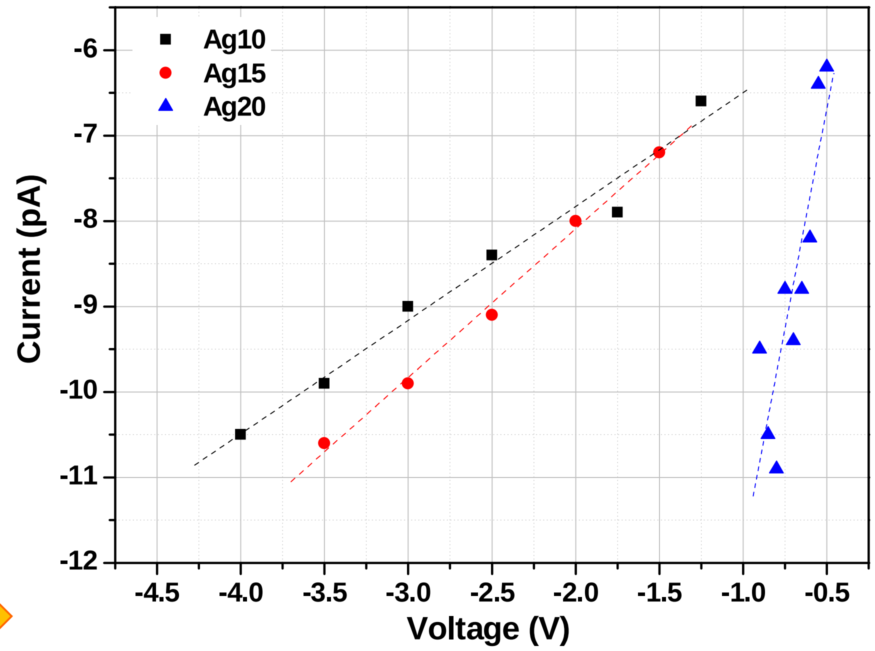
A.A. Piarristeguy, M. Ramonda, N. Frolet, M. Ribes, A. Pradel, Solid State Ionics 181 (2010) 1205-1208.

Conductivity of each phase: Conductive Atomic Force Microscopy

✓ **C-AFM**

Qualitative evaluation of conductivity

If the contact is assumed to be circular and Ohmic in nature then the relation between the resistance ***R*** *and the resistivity ρ is given by the basic spreading resistance formula* ***R ~ ρ /4r*** *where r is the radius of the contact*



For the tip radius: : r~10 nm

σ ~ 0,3 x 10^{-6} Ω^{-1}cm^{-1}

to 3 x 10^{-6} Ω^{-1}cm^{-1}

with increasing of the silver content in the samples.

A.A. Piarristeguy, M. Ramonda, N. Frolet, M. Ribes, A. Pradel, Solid State Ionics 181 (2010) 1205-1208.

Conclusion

Rôle important de la structure sur la mobilité des ions dans les verres

System : $45\ Li_2O - 55\ [x\ B_2O_3 - (1\text{-}x)\ P_2O_5)]$

Evolution non linéaire de la conductivité liée à la stabilisation des B^{IV}
en présence d'entités phosphate

System : $30\ Li_2S - 70\ [x\ SiS_2 - (1\text{-}x)\ GeS_2)]$

Augmentation de la conductivité quand Ge/Si ~ 1 due à une séparation de phase

System : $Ag_x(Ge_{0.25}Se_{0.75})_{100\text{-}x}$

Saut de conductivité de 8 ordres de grandeur due à la percolation
d'une phase riche en argent