Chalcogenide glasses compositions vs structure

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- **Chalcogenide glass formers**
  - Structure
  - Comparison oxide / chalcogenide [SiO_2/**$SiS(e)_2$**]
- **Ion conducting chalcogenide glasses (Modifier + Former)**
  - Depolymerization of glassy network (edge sharing/corner sharing tetrahedra; bridging / non bridging sulfur/selenium); ^{29}Si NMR, XPS
  - Phase separation in Ag^+ conducting chalcogenide glasses; Near field microscopy
- **Mixed Glass Former Effect**

  Heterogeneous versus homogeneous mixing; **Li_2S-SiS_2-GeS_2**; Raman, SAXS
- **Mixed Alkali Effect**

  Cation distribution in the glassy network; Li_2S-Na_2S-GeS_2; REDOR NMR

  Cation environment and glassy network rearrangement; Ag_2S-Rb_2S-GeS_2; Raman, EXAFS, SAXS
- **Conclusions**

Chalcogenide glass formers — **Role of chalcogen on the structure**

Homologous to SiO_2 and GeO_2 –stoichiometric glasses

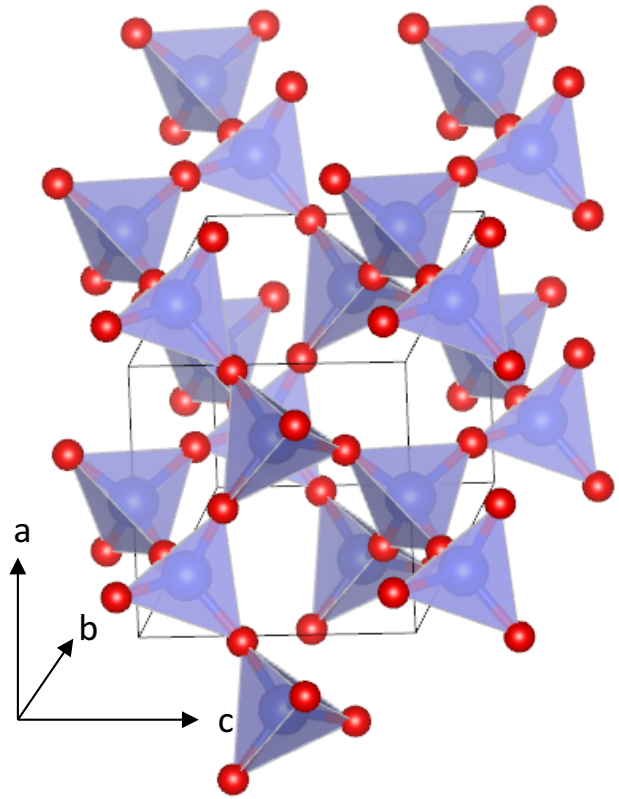
$SiS(e)_2$, $GeS(e)_2$

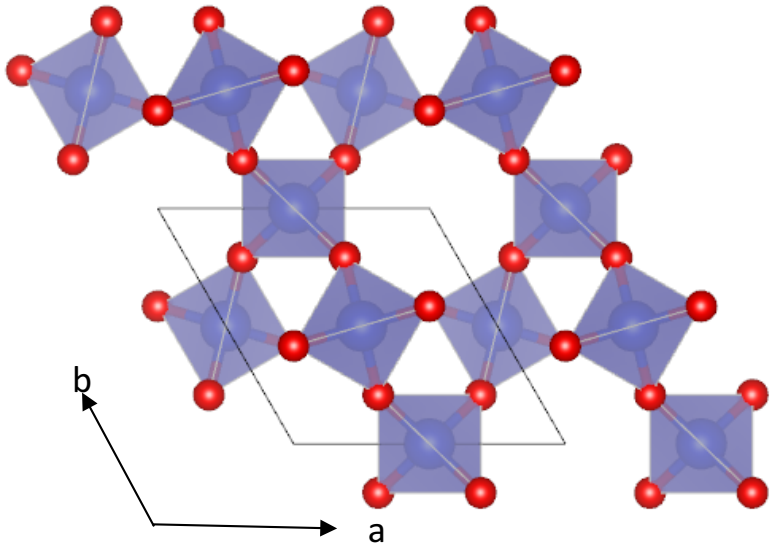
Ia												IIIa	IVa	Va	VIa	VIIa	0
1 H	IIa																2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg	IIIb	IVb	Vb	VIb	VIIB	VIIIb			Ib	IIb	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 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

Role of chalcogen on the structure

SiO_2 Quartz





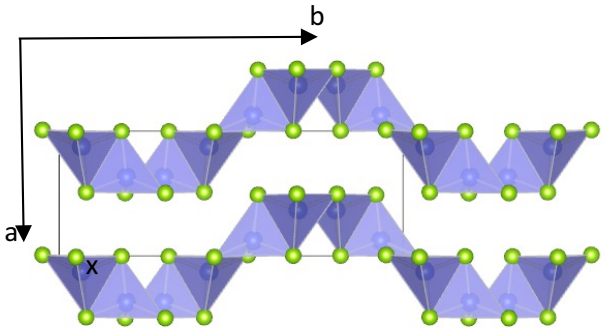
Projection 001

3D-structure. Each (SiO_4) Td shares its 4 corners with 4 neighbouring Td

Chalcogenide glass formers

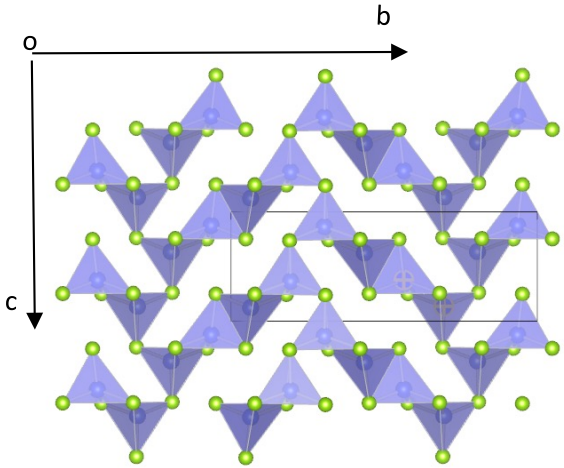
Role of chalcogen on the structure

$SiSe_2$ Low Temperature form

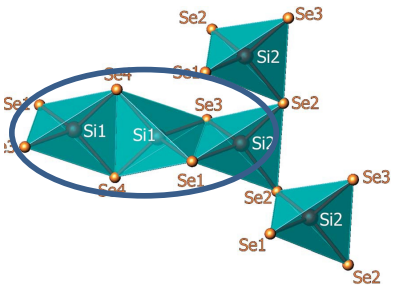


Projection 001

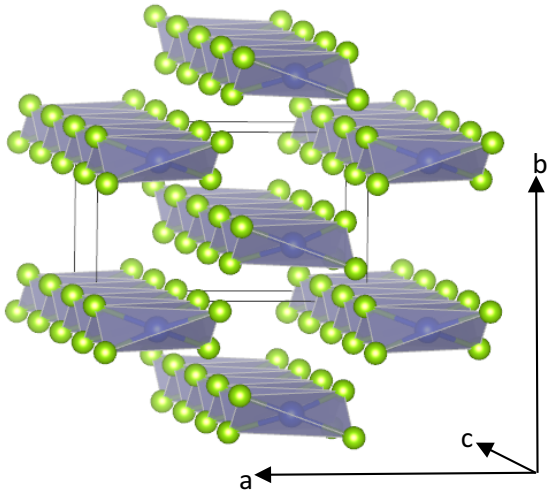
Blocks of edge sharing Td
These « blocks » are linked together by corners :
a complex structure



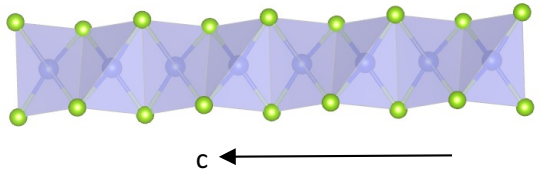
Projection 100



SiS_2, $SiSe_2$ High Temperature form



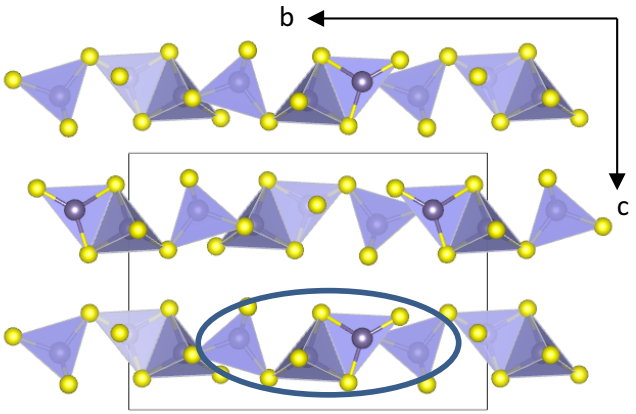
Chains of edge-sharing Td
1D-structure



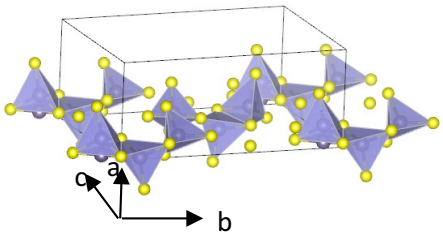
Chalcogenide glass formers

Role of chalcogen on the structure

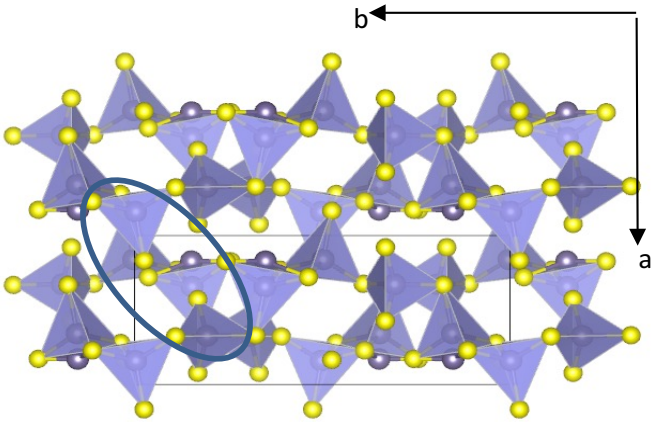
GeS_2 β (High temperature form)



Projection 100

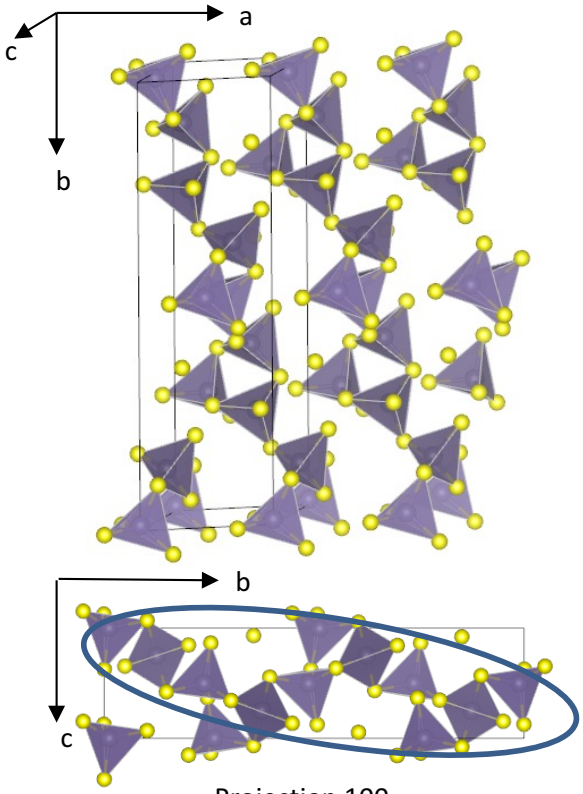


2D-structure.
A plan comprises chains of edge and corner sharing Td (projection (100)).
These chains are connected by corners (projection (001))



Projection 001

GeS_2 α (Low temperature form)



Projection 100

3D-structure.
Each Td shares its 4 corners with 4 neighbouring Td

Chalcogenide glass formers — **Role of chalcogen on the structure**

Zachariasen enounced 4 rules to define what is a glass former (in oxides)

Rule # 3 : **constituting polyhedra should share only corners !**

As a matter of fact, GeS_2 can be obtained rather easily (air quenching);
$SiS(e)_2$ require fast quenching

Smekal model : **co-existence of different types of forces**

Van der Waals + covalent

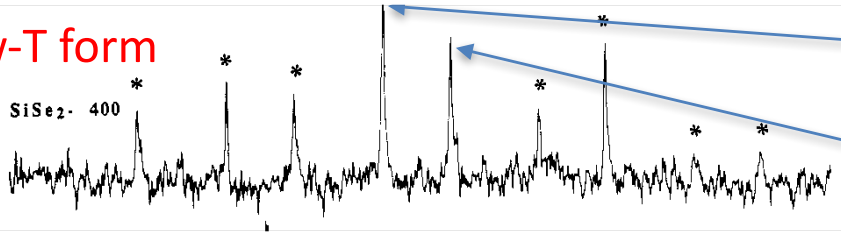
Role of chalcogen on the structure

^{29}Si MAS NMR

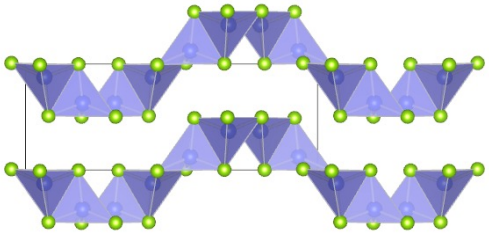
Crystalline $SiSe_2$

E_2 = Td with 2 edges shared with neighbours
E_1 = Td with 1 edge shared with neighbours
E_0 = Td with no edge shared with neighbours (corner sharing Td)

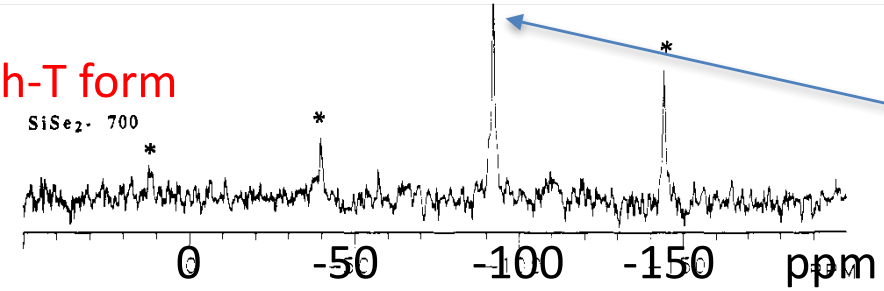
Low-T form



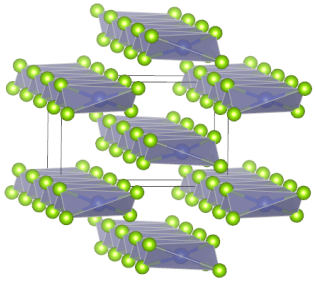
E^1 + E^2



High-T form



E^2



* Rotation bands

Role of chalcogen on the structure

^{29}Si MAS NMR

Crystalline $SiSe_2$

E_2 = Td with 2 edges shared with neighbours
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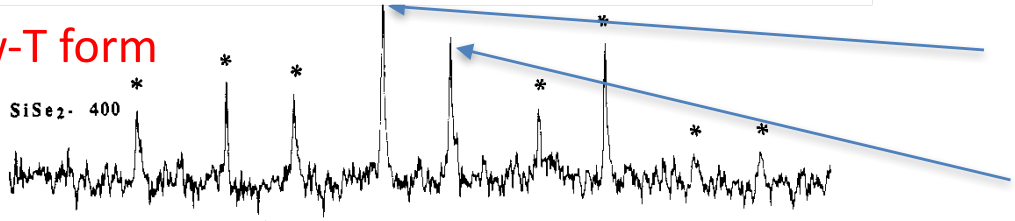
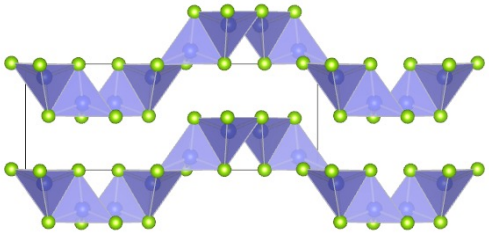
E_0 = Td with no edge shared with neighbours (corner sharing Td)

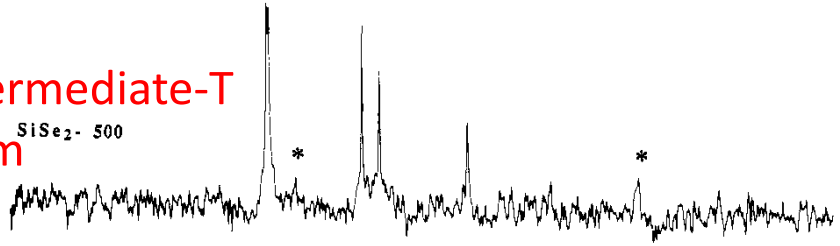
Low-T form



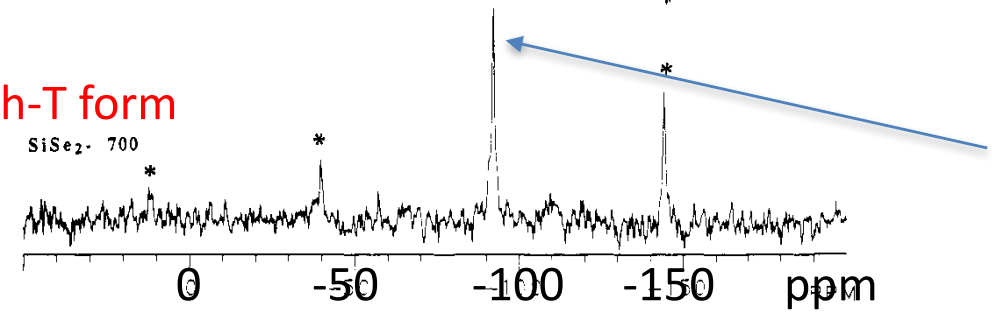
E^1 + E^2



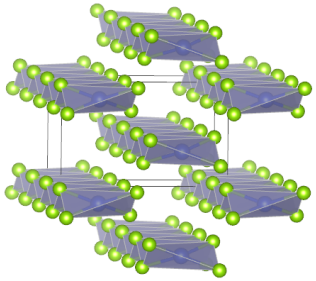
Intermediate-T form



High-T form



E^2



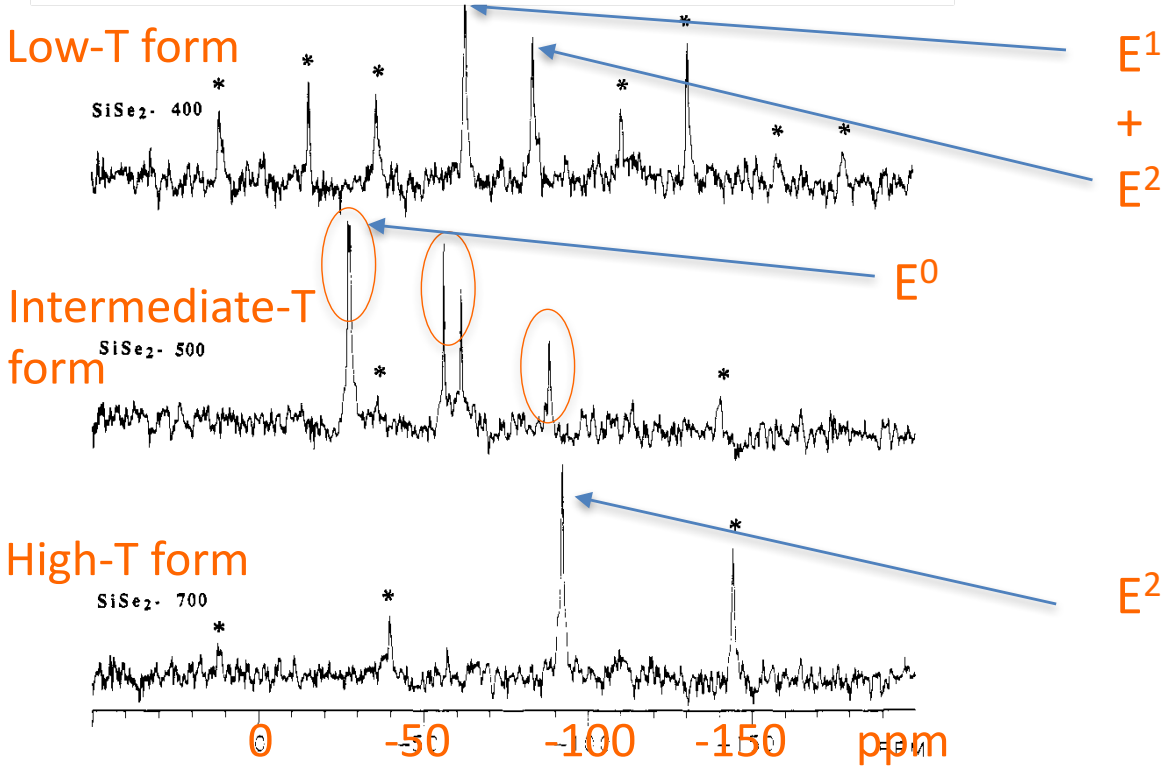
* Rotation bands

Role of chalcogen on the structure

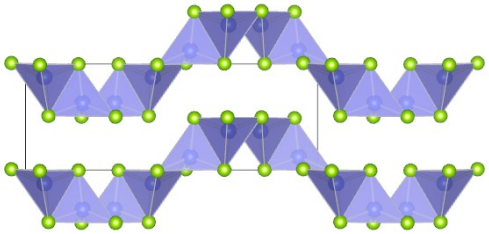
^{29}Si MAS NMR

Crystalline $SiSe_2$

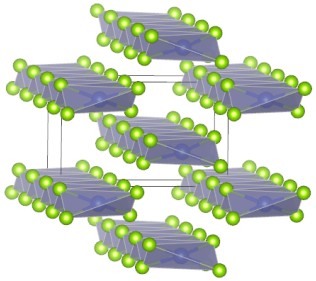
E_2 = Td with 2 edges shared with neighbours
E_1 = Td with 1 edge shared with neighbours
E_0 = Td with no edge shared with neighbours (corner sharing Td)

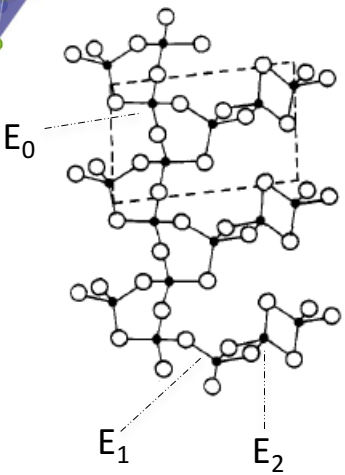


* Rotation bands



Structure unsolved



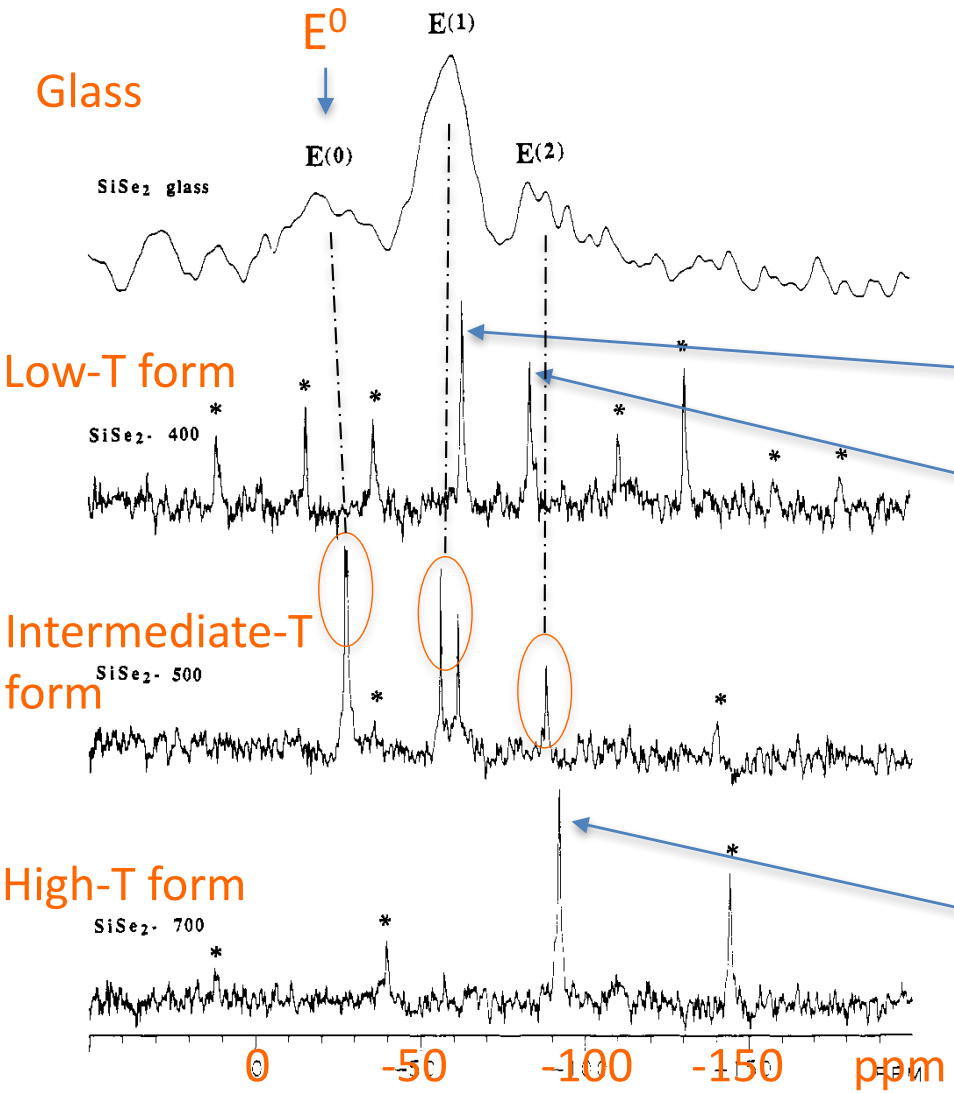


Chalcogenide glass formers

Role of chalcogen on the structure

^{29}Si MAS NMR

Glass $SiSe_2$

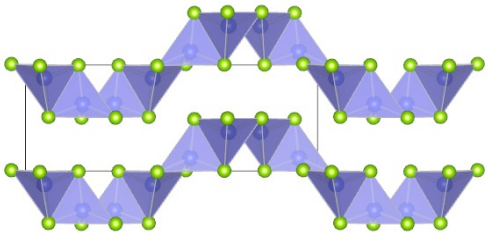


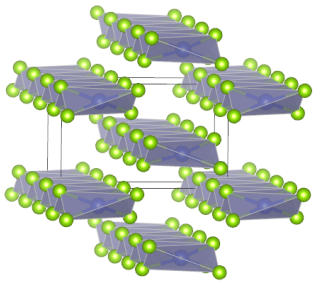
E^1 + E^2

E^2

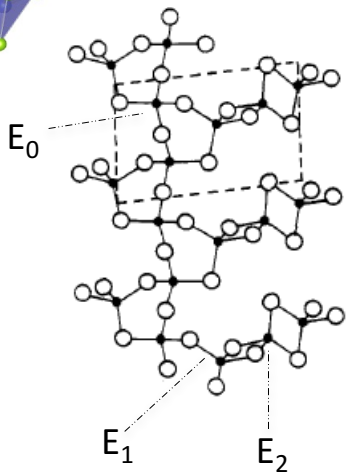
* Rotation bands

E_2 = Td with 2 edges shared with neighbours
E_1 = Td with 1 edge shared with neighbours
E_0 = Td with no edge shared with neighbours (corner sharing Td)



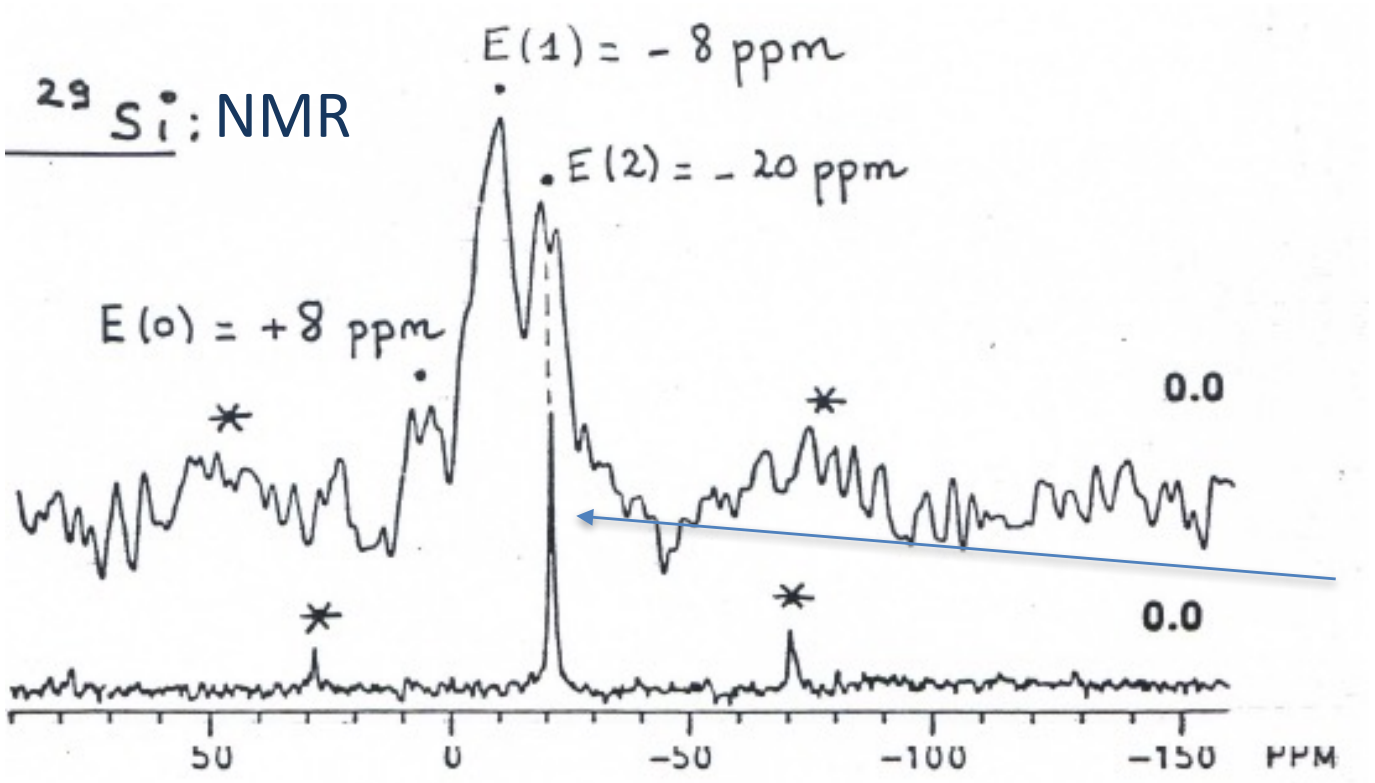


Structure unsolved

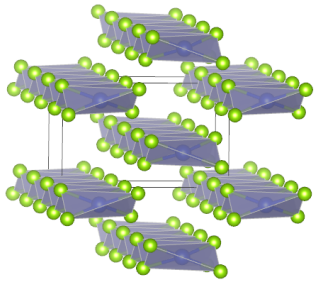


Chalcogenide glass formers — Role of chalcogen on the structure

Glass SiS_2



E^2



Chemical shifts amplitude : 28 ppm

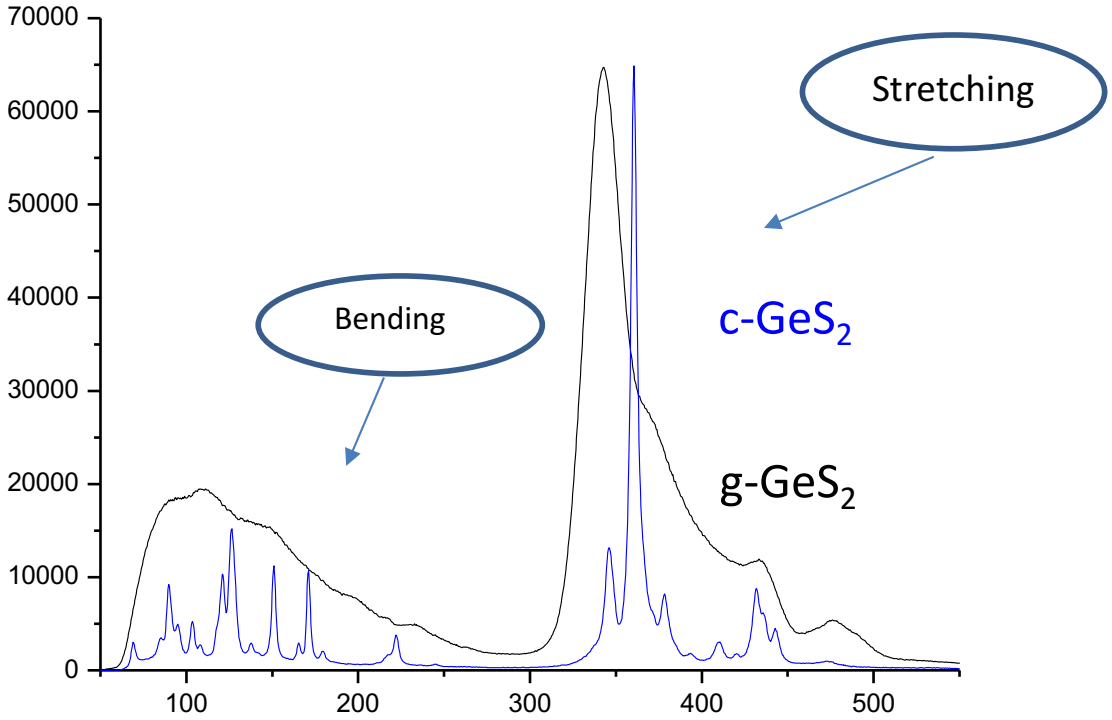
against 62 ppm in the case of selenide glasses

Chalcogenide glass formers

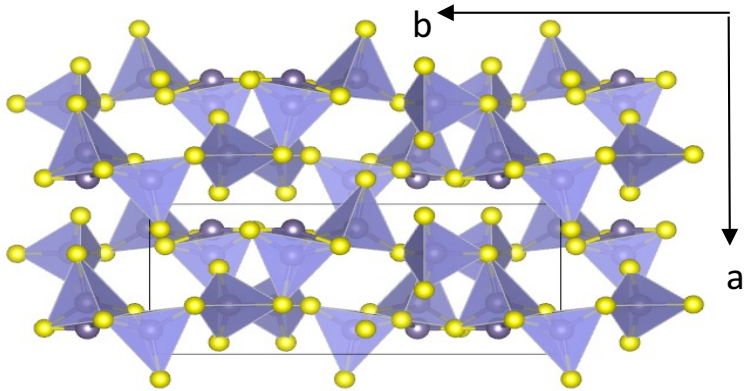
Role of chalcogen on the structure

Glass GeS_2

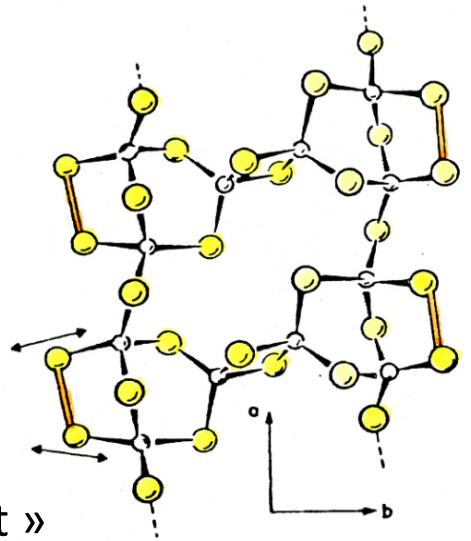
Raman spectra



GeS_2 β (High temperature form)



Projection 001



« outrigger raft » model

Chalcogenide glass formers

To summarize

Co-existence of corner-sharing tetrahedra and edge-sharing tetrahedra

Predominance of edge-sharing Td for $SiS(e)_2$

Predominance of corner-sharing Td for $GeS(e)_2$

^{29}Si NMR E^0 E^1 E^2

Modified chalcogenide glasses

Role of modifier on the structure

$SiS(e)_2$

+

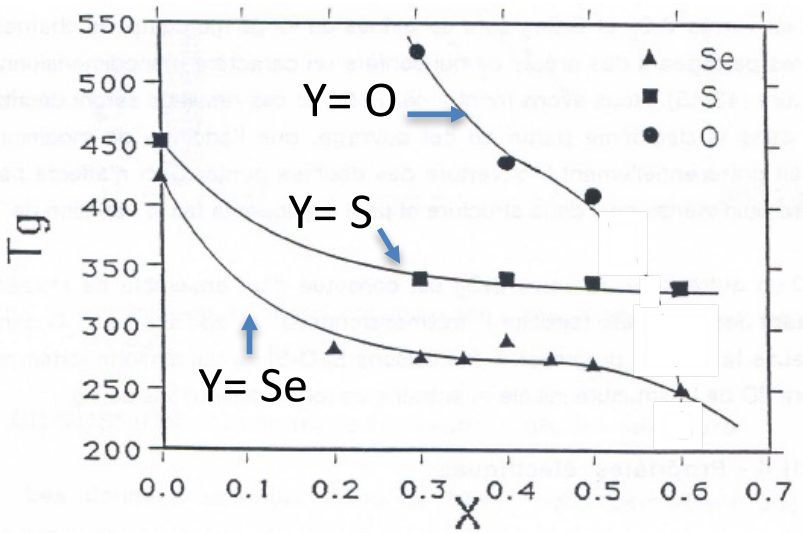
$M_2S(e)$

M = Li, Na, Ag

Modified chalcogenide glasses

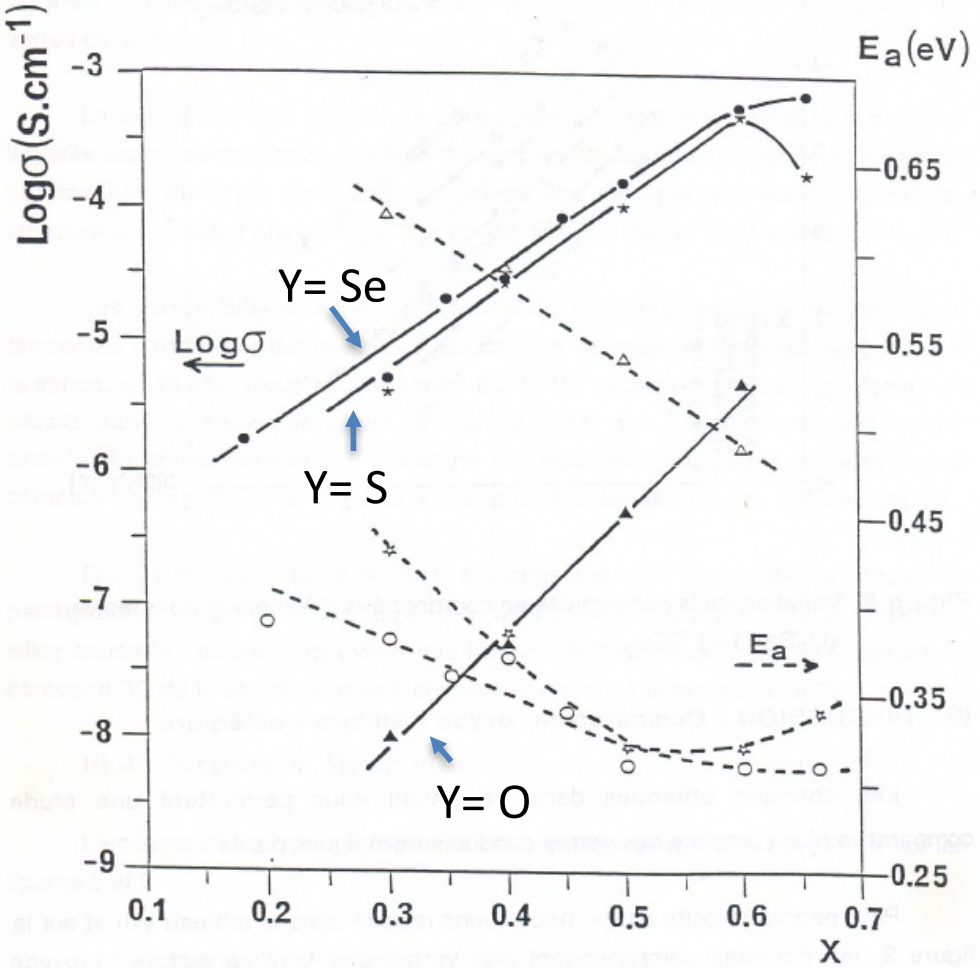
System $xLi_2Y-(1-x)SiY_2$, Y = O, S, Se

Vitreous transition temperature



Large decrease in Tg for the first addition of alkali

Conductivity and Activation Energy



Conductivity in chalcogenides much larger than in oxide (2.5 orders of magnitude)

Large increase in ion conductivity with addition of alkali ions
(Li content x 2 → Gain of 2 orders of magnitude in conductivity)

For oxide glasses

Role of modifier on the structure

SiO_2

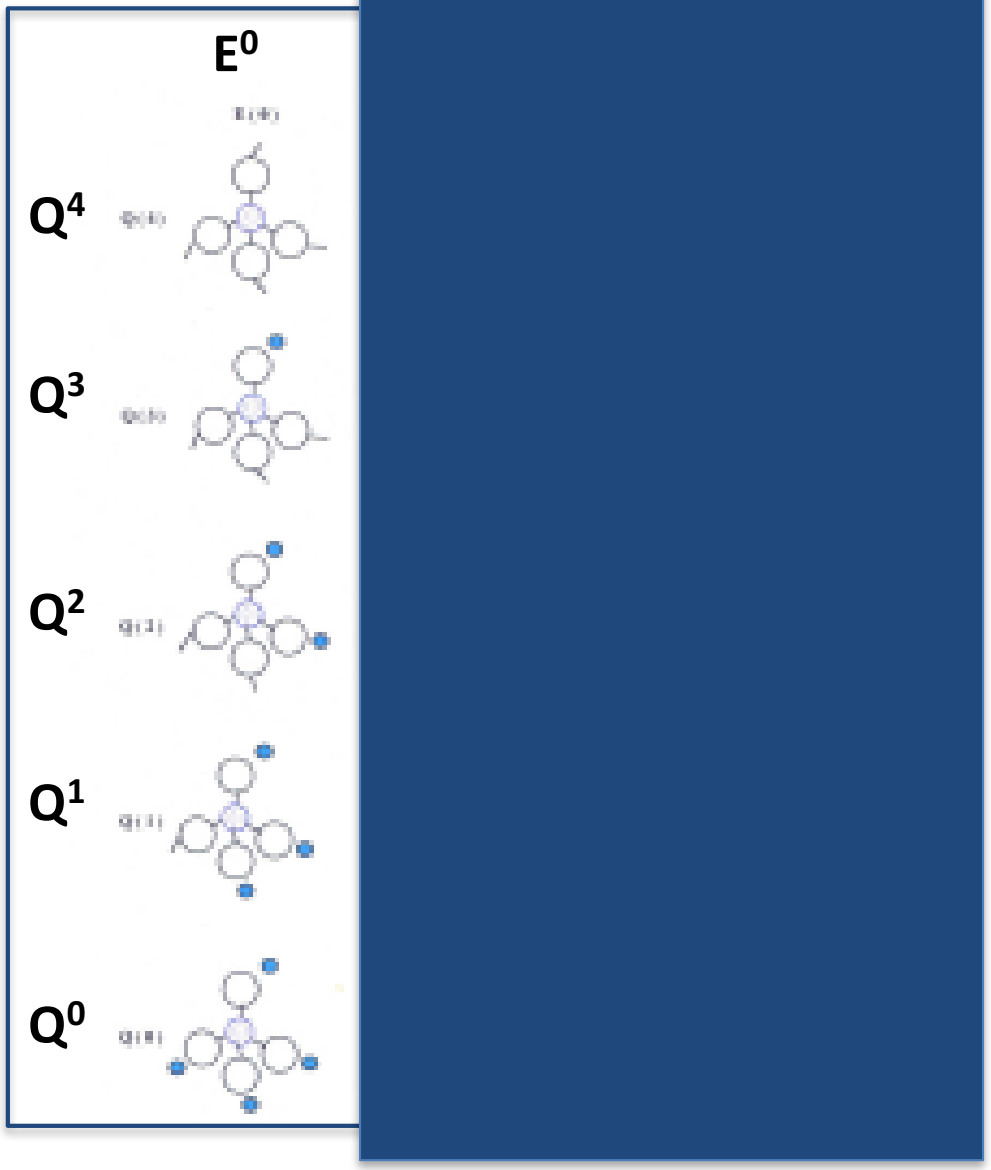
+

M_2O

M = Li, Na, Ag

Creation of non bridging oxygen

Entités Q^n



Modified chalcogenide glasses

Role of modifier on the structure

$SiS(e)_2$

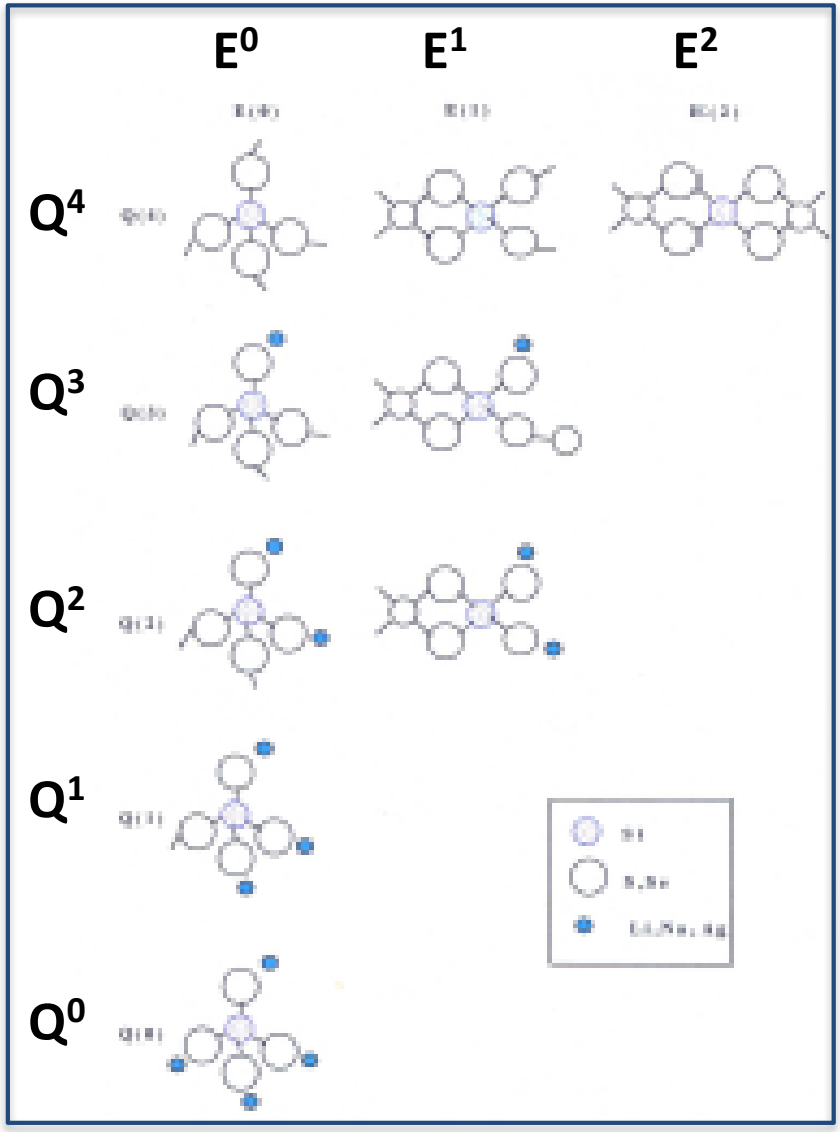
+

$M_2S(e)$

M = Li, Na, Ag

Creation of non bridging sulfur

E^nQ^n Entities



Modified chalcogenide glasses

Role of modifier on the structure

1st step

Identification of crystalline phases; identification of their E^nQ^n building entities

Identification of corresponding chemical shifts in ^{29}Si NMR spectra

2nd step

Obtention of ^{29}Si NMR spectra of corresponding glassy compositions

Identification of their E^nQ^n building entities by comparison with NMR spectra of crystalline phases

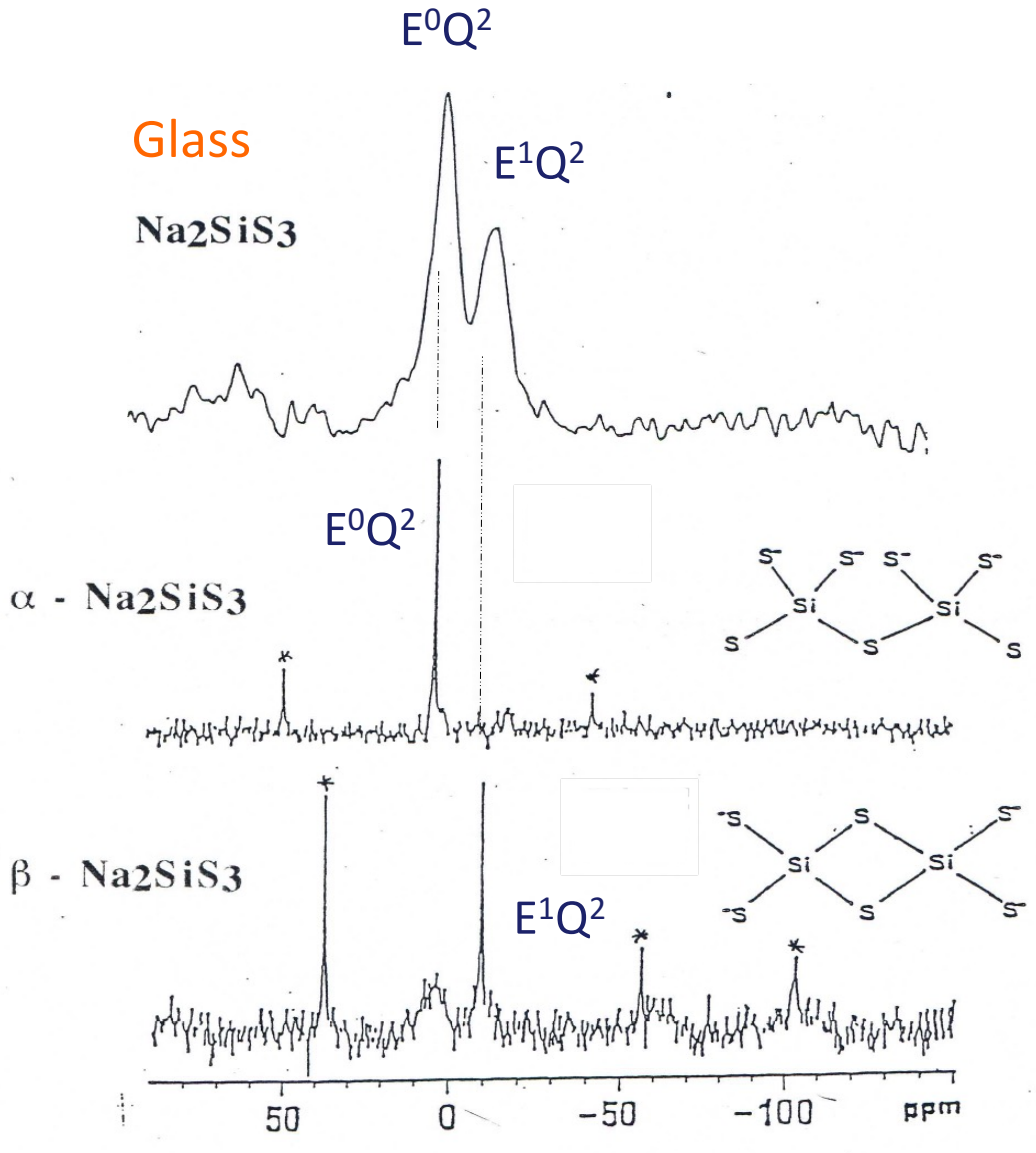
Role of modifier on the structure

Modified chalcogenide glasses

System xNa_2S- $(1-x)SiS_2$

X = 0.5

Na_2SiS_3 glass contains both E^1 and E^0 entities



Role of modifier on the structure

Modified chalcogenide glasses

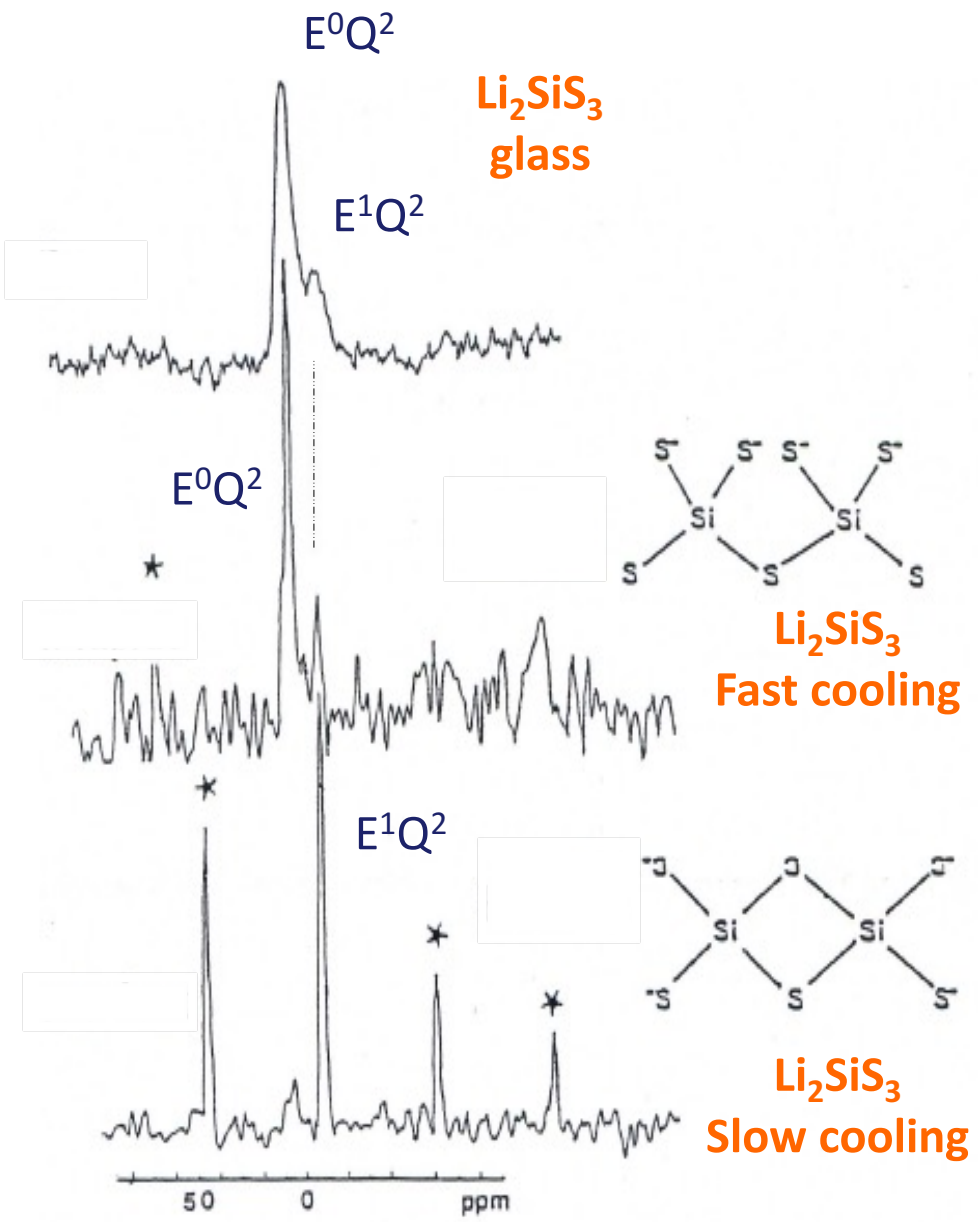
+

Crystalline compounds

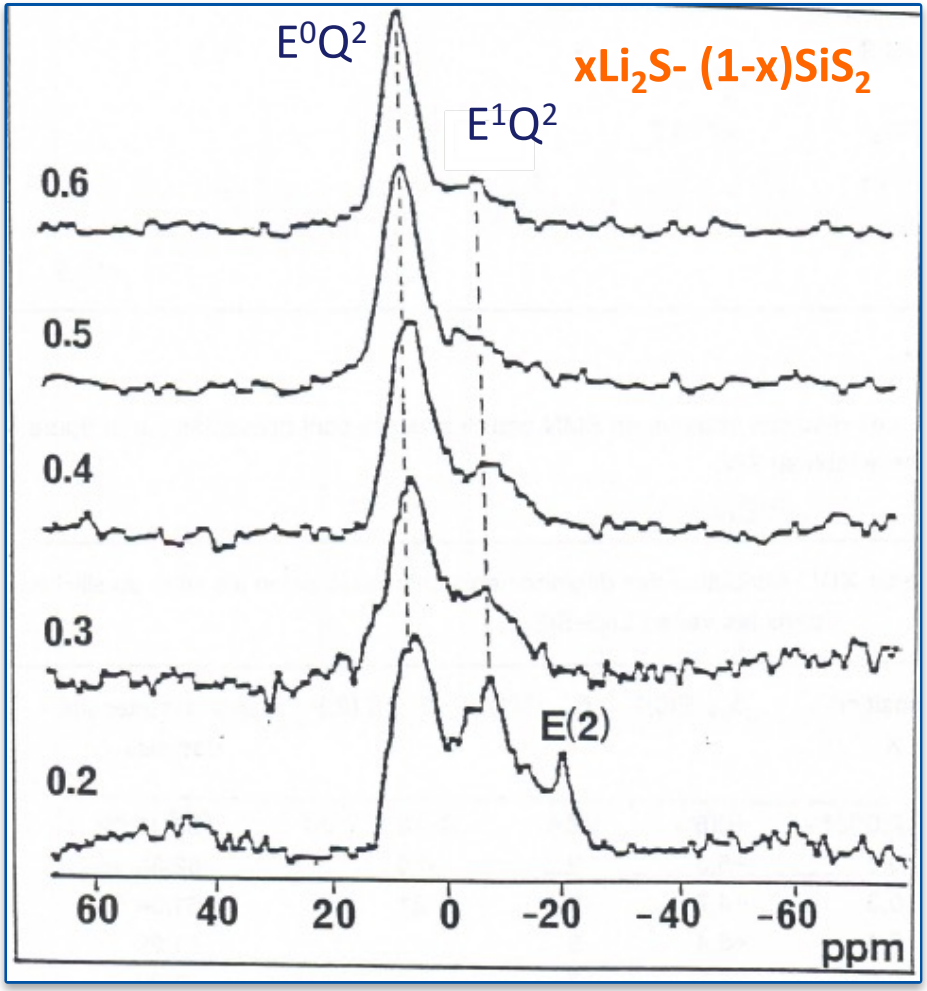
System xLi_2S- $(1-x)SiS_2$

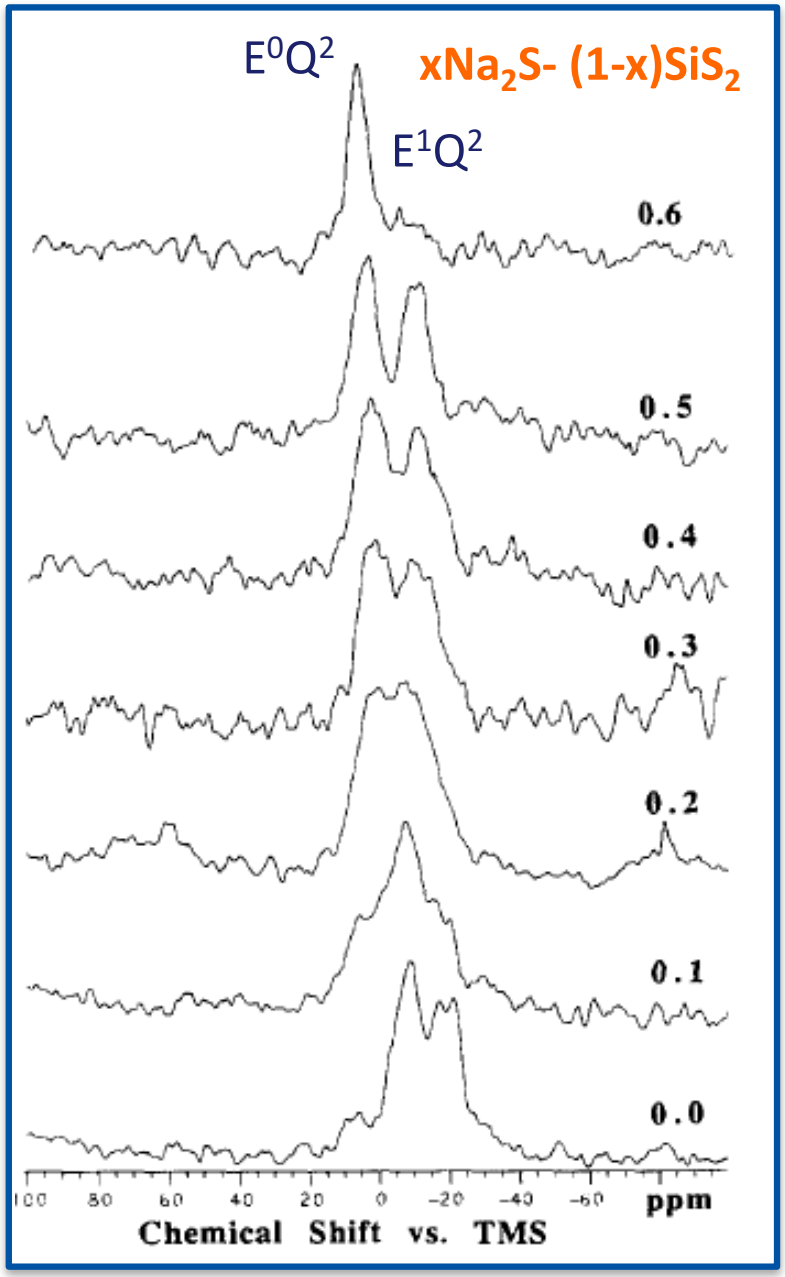
X = 0.5

Li_2SiS_3 glass contains
both E^1 and E^0 entities
BUT
25% E^1 only



Preferential destruction of edge-sharing tetrahedra in the case of Li-glasses



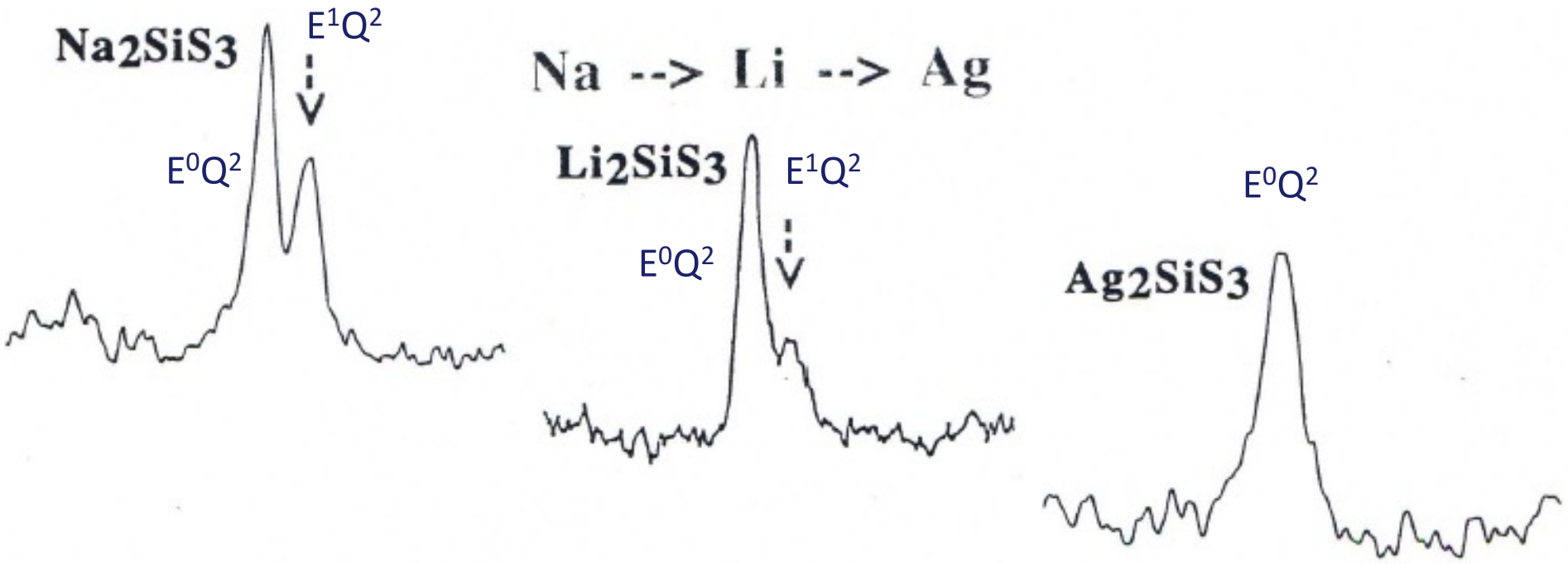


Modified chalcogenide glasses

Role of modifier on the structure

System xM_2S- $(1-x)SiS_2$ with M = Li, Na, Ag

X = 0.5

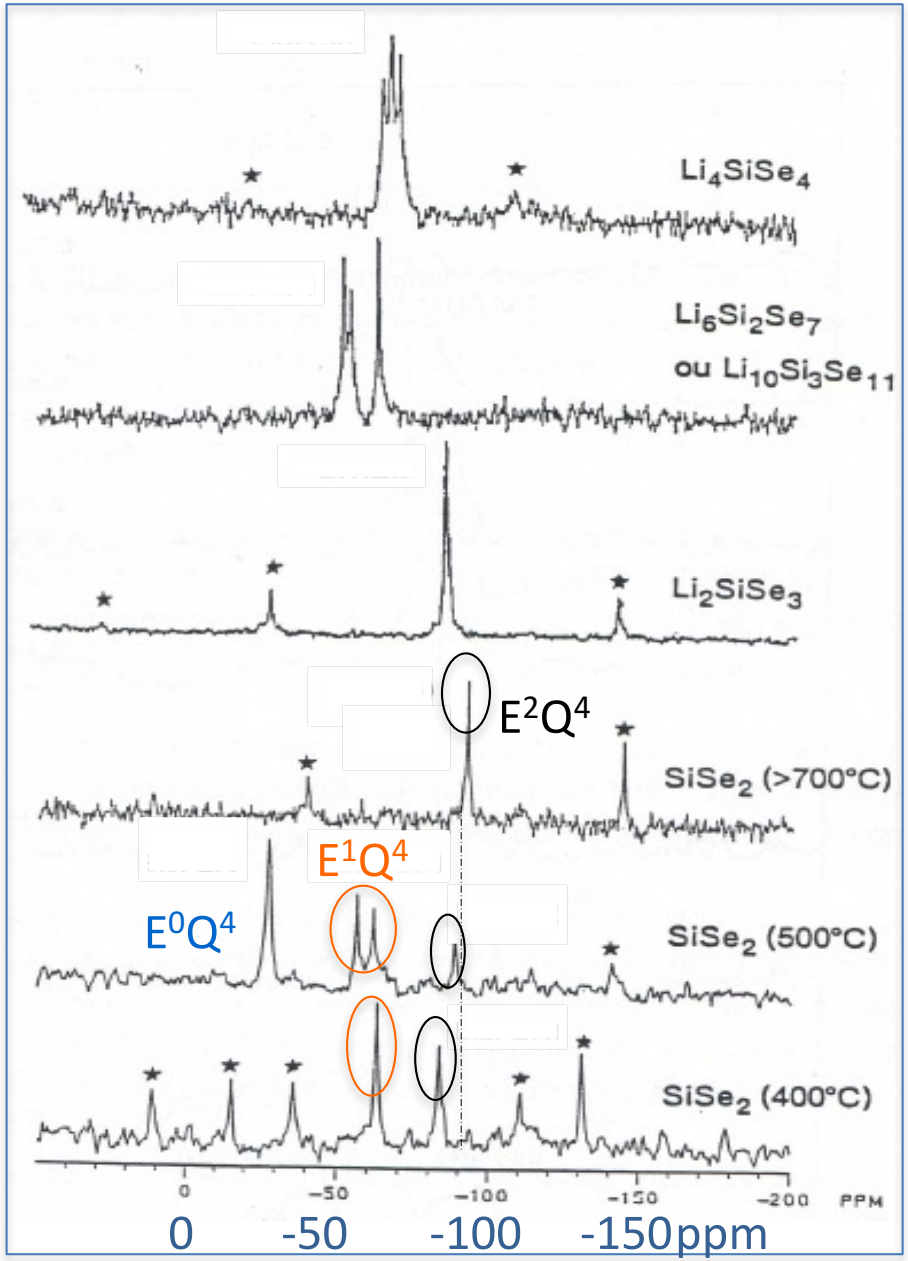


Preferentiel destruction of edge-sharing tetrahedra in any case, increasing from Na to Li to Ag

Role of modifier on the structure

Investigation of crystalline phases in the system $xLi_2Se- (1-x)SiSe_2$

chemical shifts
between different E^2Q^4 units
($SiSe_2$ high, intermediate and low T)
and
between different E^1Q^2 units
(2 E^1Q^2 sites in intermediate T $SiSe_2$
+ 1 E^1Q^2 site in low T $SiSe_2$)

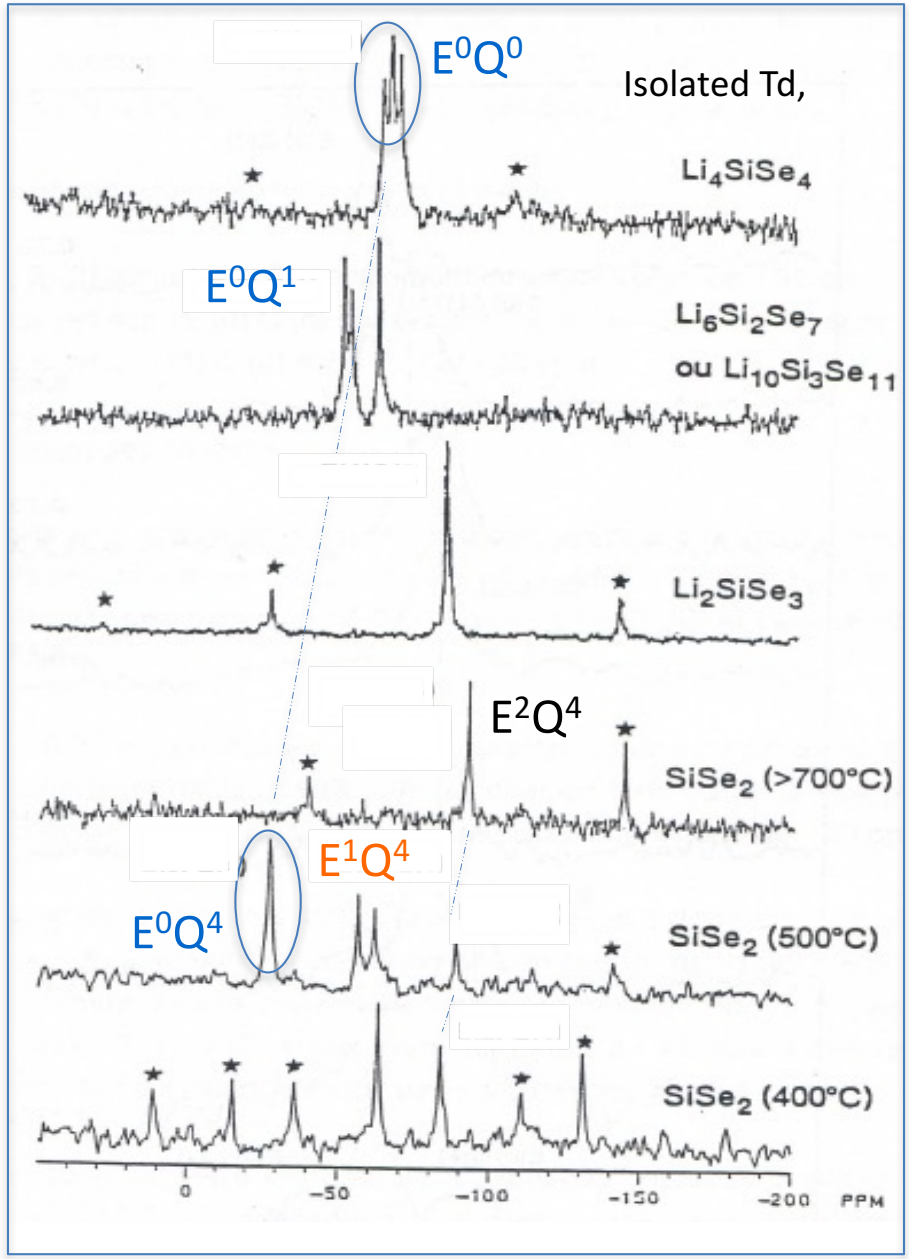


Role of modifier on the structure

Investigation of crystalline phases in the system $xLi_2Se-(1-x)SiSe_2$

large chemical shifts
between different E^0Q^n units
(E^0Q^4 site in intermediate-T $SiSe_2$
+ E^0Q^0 site in Li_4SiSe_4
+ E^0Q^1 sites in $Li_6Si_2Se_7$ ($Li_{10}Si_3Se_{11}$)

^{29}Si NMR sensitive to Qn entities in selenides

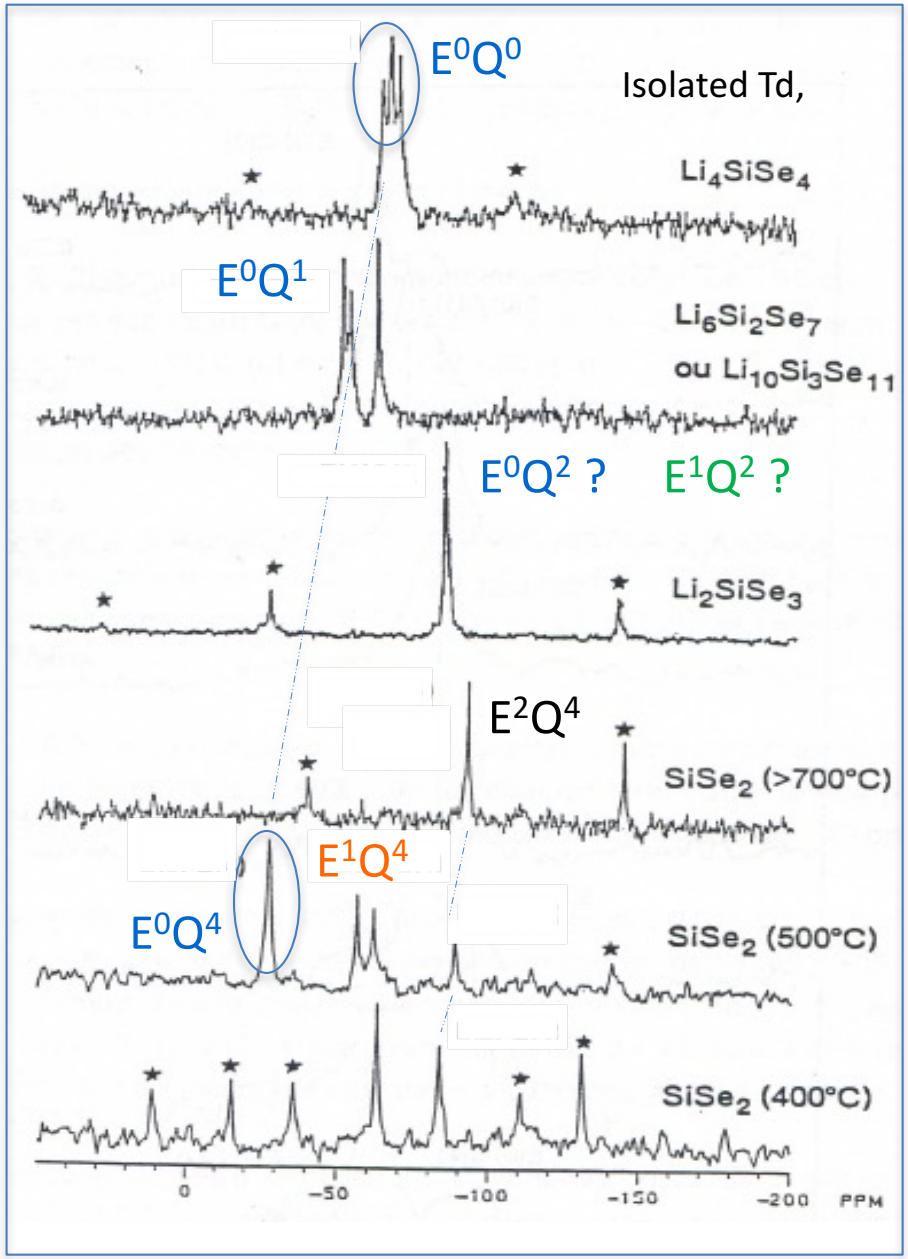


Role of modifier on the structure

Investigation of crystalline phases in the system xLi_2Se- $(1-x)SiSe_2$

Which units for Li_2SiSe_3
E^0Q^2 or E^1Q^2
??

^{29}Si NMR sensitive to Qn entities in selenides

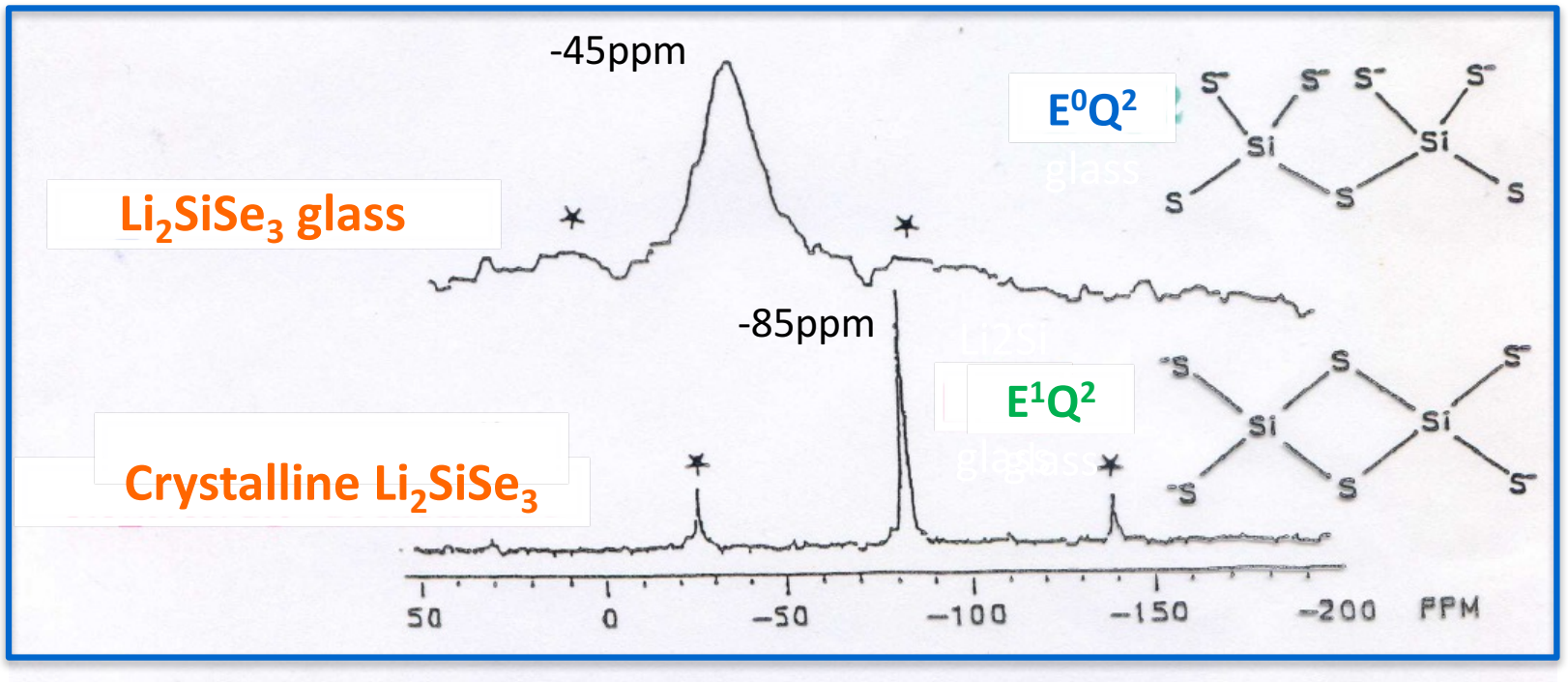


Role of modifier on the structure

Modified chalcogenide glasses

Investigation in the system xLi_2Se- $(1-x)SiSe_2$

X = 0.5



Which units for Li_2SiSe_3

E^0Q^2 or E^1Q^2

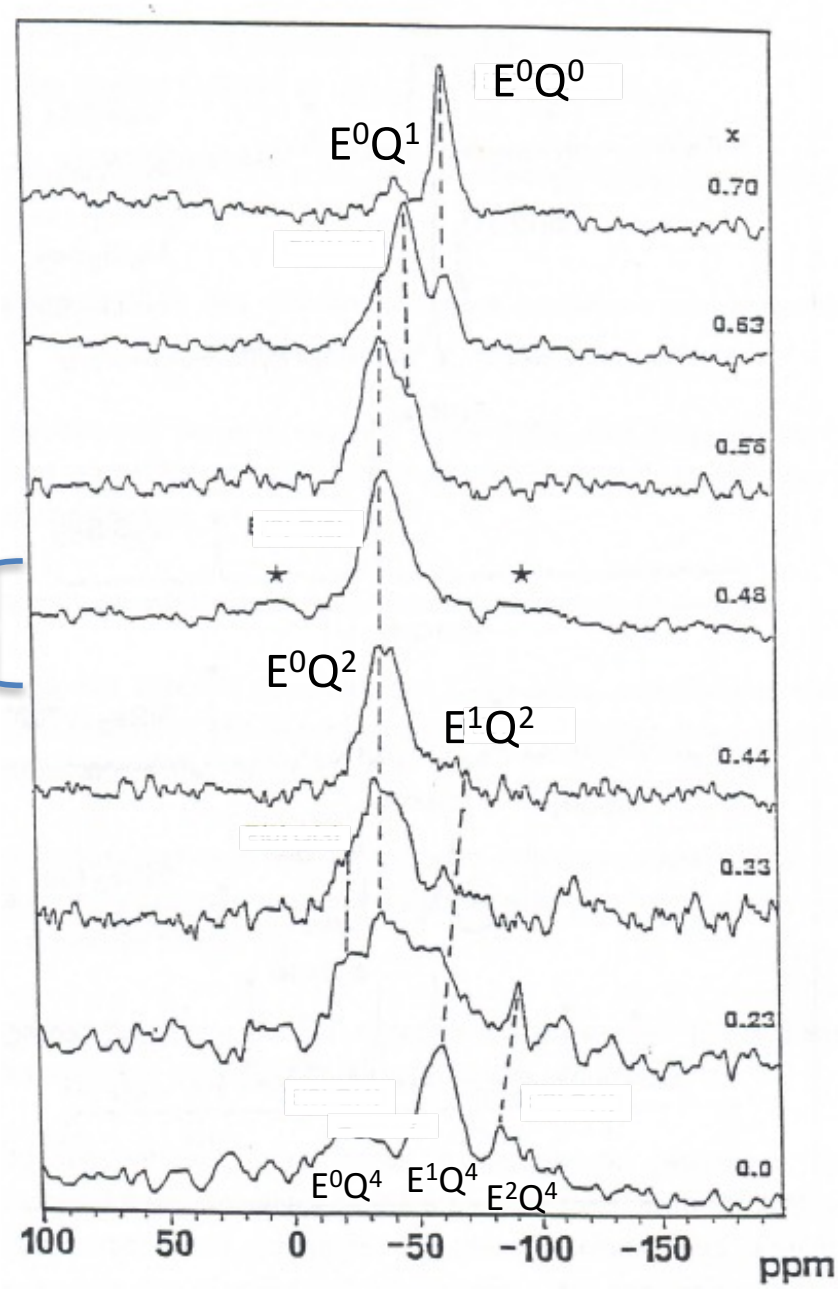
??

Role of modifier on the structure

Modified chalcogenide glasses

$xLi_2Se- (1-x)SiSe_2$ glasses

X = 0.48
No more E^1



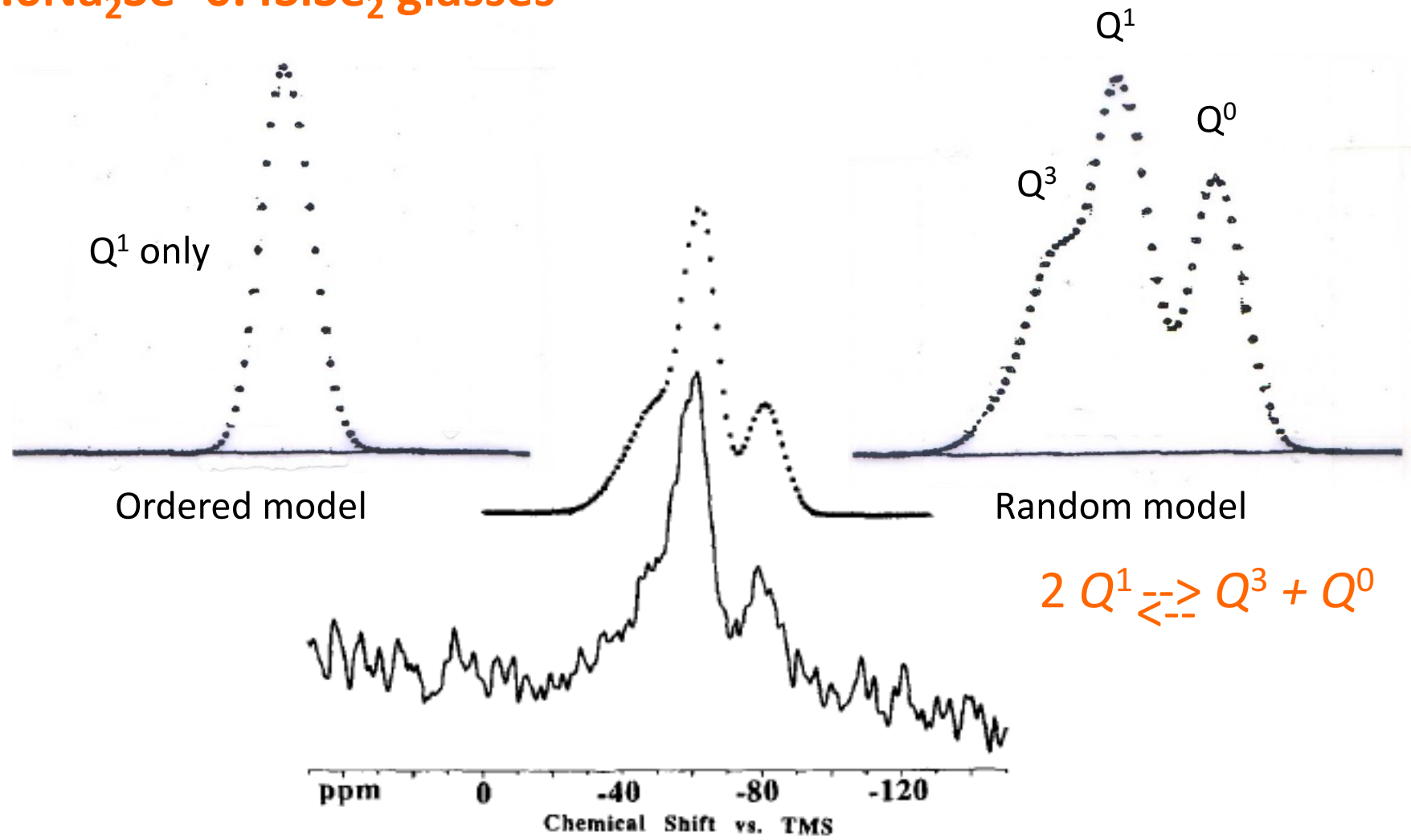
Li_2Se tends to destroy edge-sharing tetrahedra preferentially

Stronger trend than in sulfides (25% E^1 left for x = 0.5)

Role of modifier on the structure

Modified chalcogenide glasses

$0.6Na_2Se- 0.4SiSe_2$ glasses



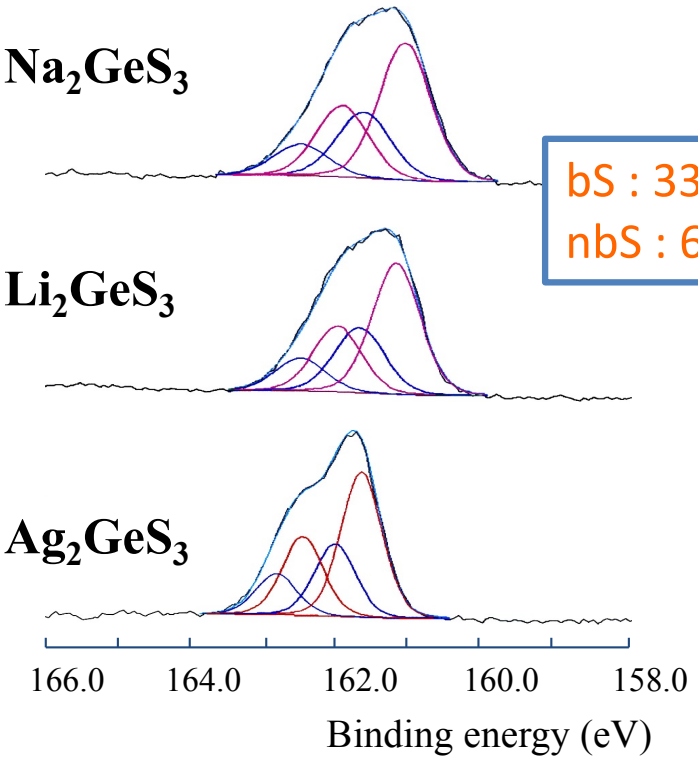
$2\ Q^1 \leftrightarrow Q^3 + Q^0$

Distribution of non-bridging Se sites is closer to random than to ordered

Role of modifier on the structure

XPS investigation

S_{2p} core peaks for M_2GeS_3 glasses; M = Ag, Li, Na



bS : 33% [33%]
nbS : 67% [67%]

Splitting
between nbS and bS

Ag : 0.5 eV
Li : 0.8 eV
Na : 0.8 eV

more homogeneous electronic distribution on sulfur atoms in the silver glass

$\Delta[E_b(Ge3p)-E_b(S2p)]$		
Ag_2GeS_3	0.6 eV	a much more important electronic redistribution
Li_2GeS_3	0.8 eV	along Ge-S bonds when the modifier cation
Na_2GeS_3	1.2 eV	changes from Ag to Na

Modified chalcogenide glasses

To summarize

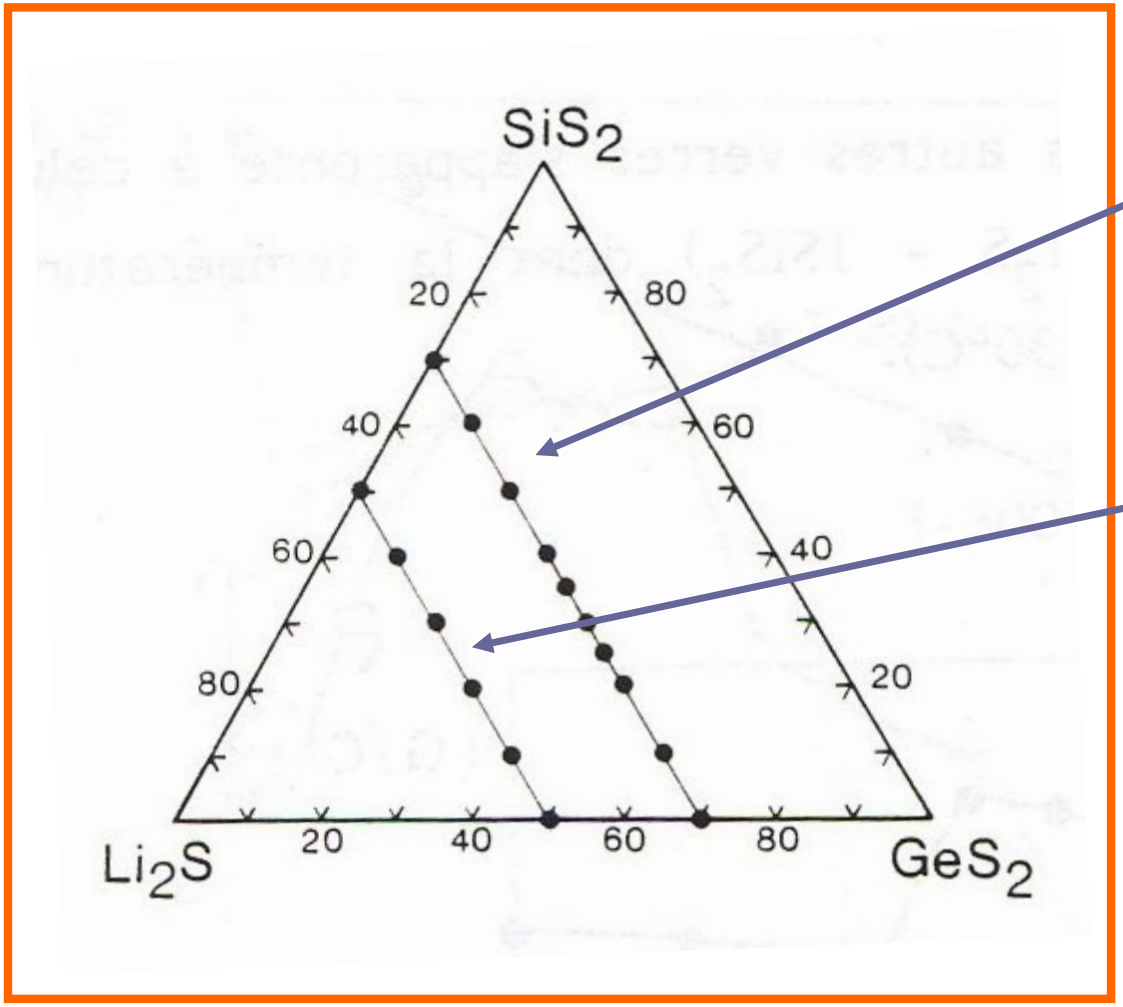
Existence of bridging and non-bridging S(e)

Trend to the destruction of edge-sharing Td increasing from Na to Li to Ag

Random distribution of modifier cations on the Td

Mixed glass former effect

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



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

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

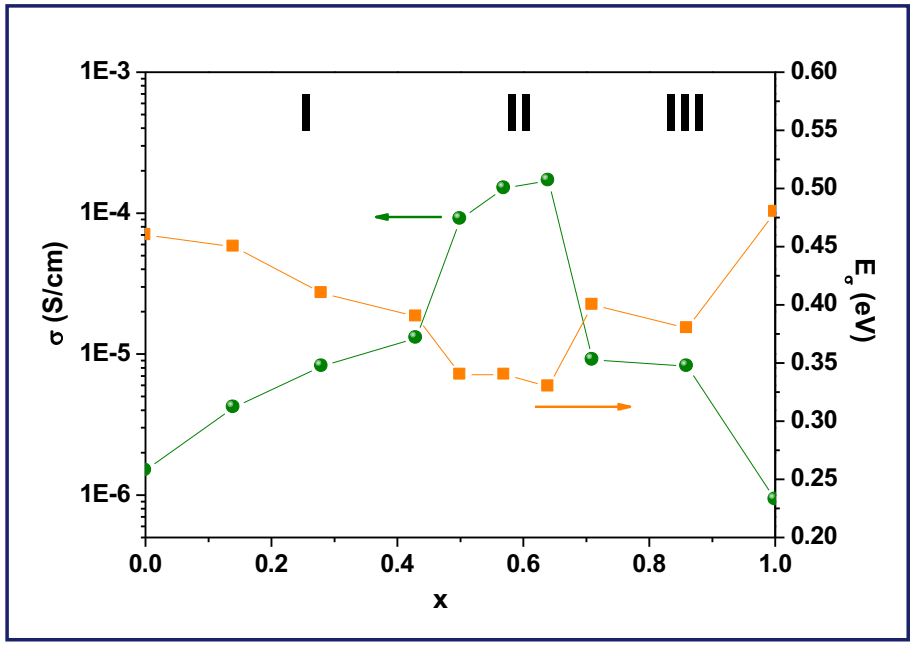
Mixed glass former effect

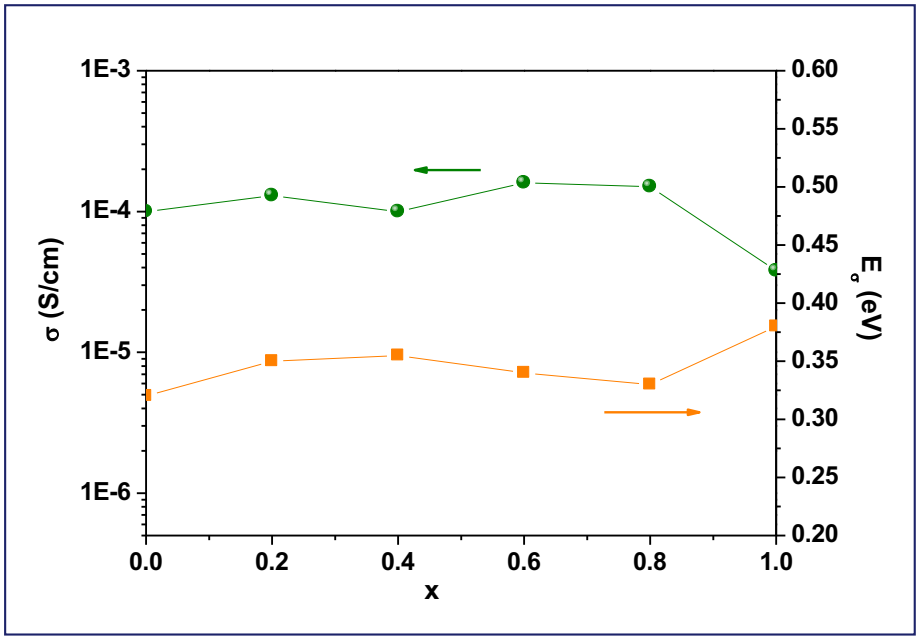
System Li_2S- [(1-x)SiS_2-xGeS_2]

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

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

Conductivity and E_s





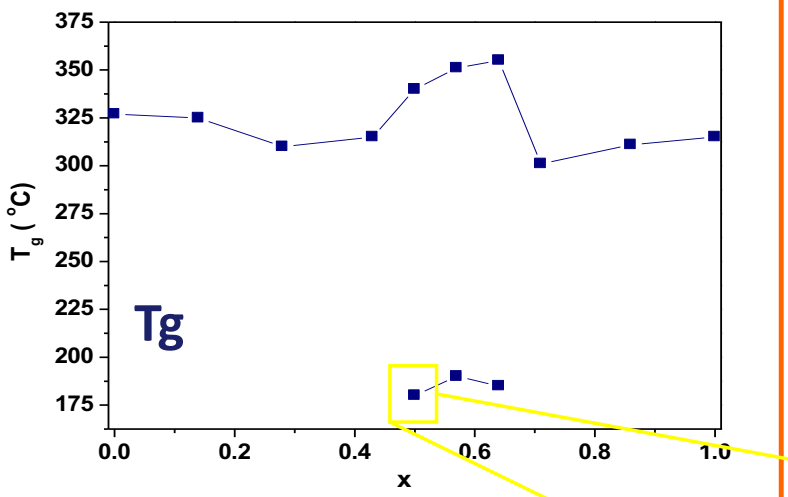
Maximum in σ and minimum in activation energy for ~ 50:50 ratio in former content

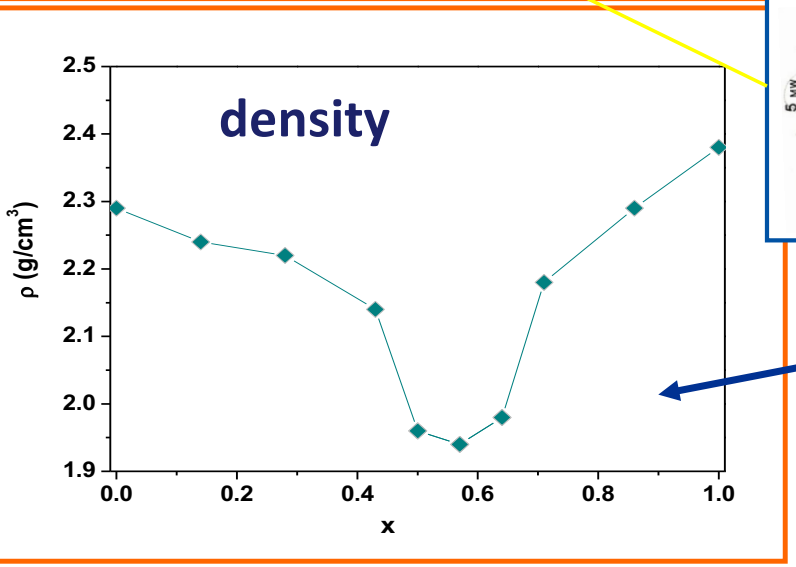
Smooth change in both σ and activation energy

Mixed glass former effect

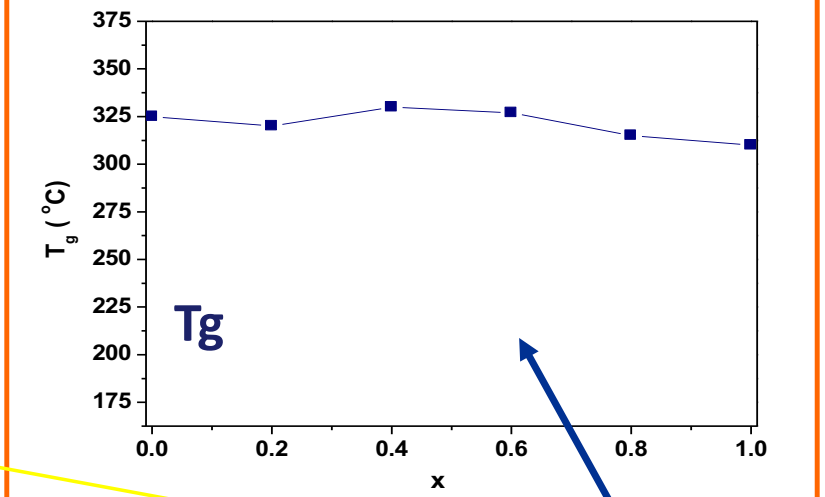
System Li_2S- [(1-x)SiS_2-xGeS_2]

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

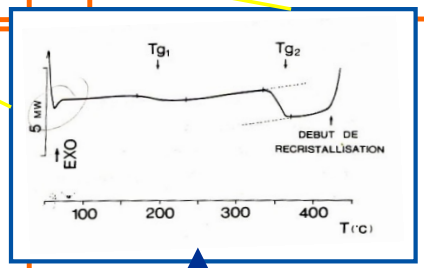




0.5 Li_2S 0.5[(1-x)SiS_2 xGeS_2]



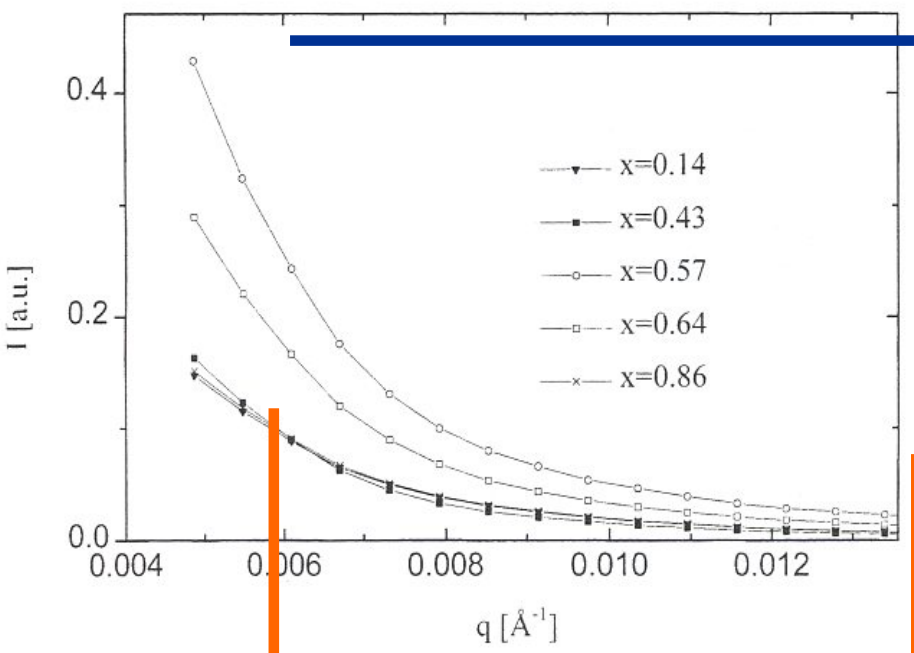
Smooth change in T_g



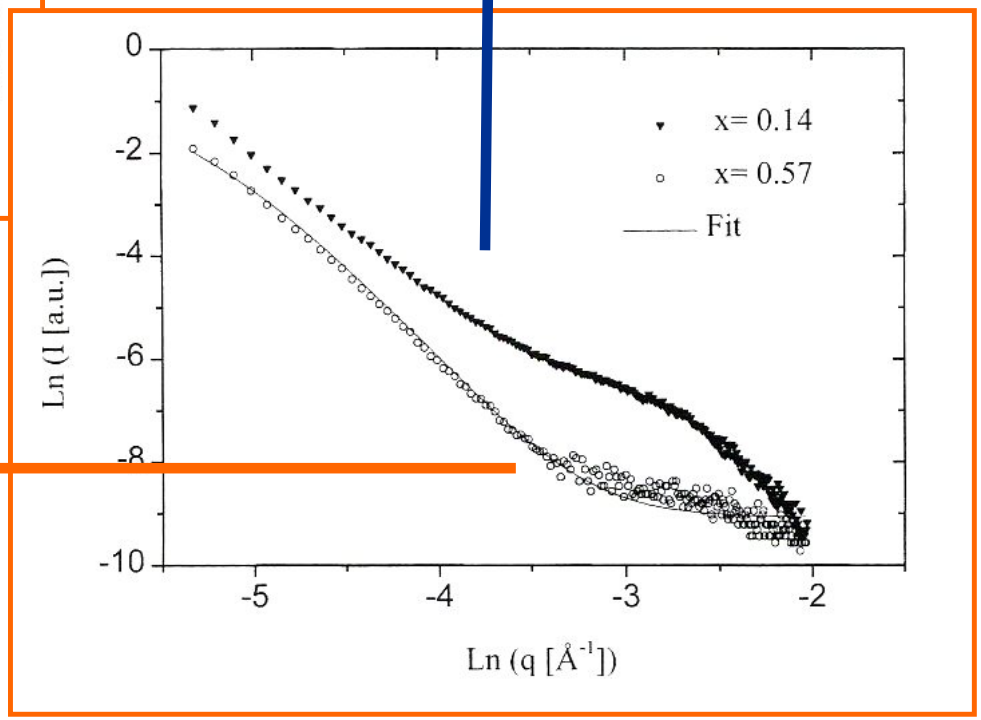
2 T_g and a minimum in ρ for ~50:50 ratio in former content

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

SAXS



Porod Law:
aggregates or clusters of 50 Å in size



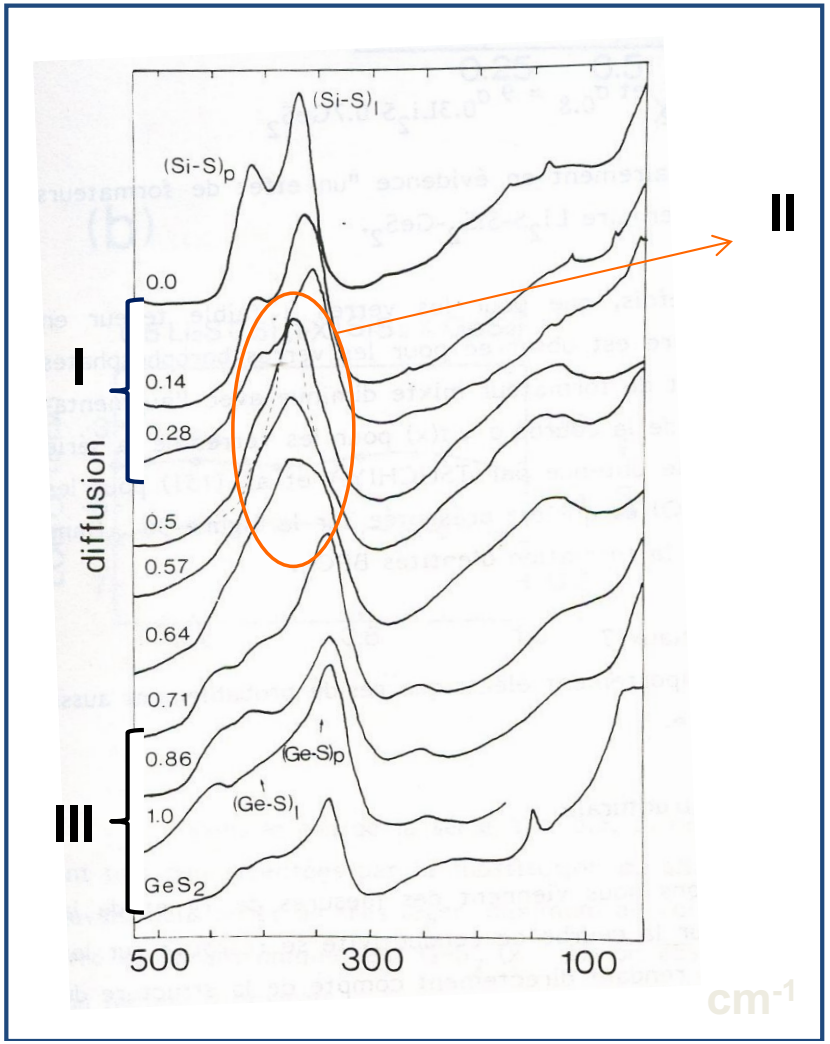
Debye-Bueche model:
homogeneous glasses

Mixed glass former effect

Raman Spectroscopy

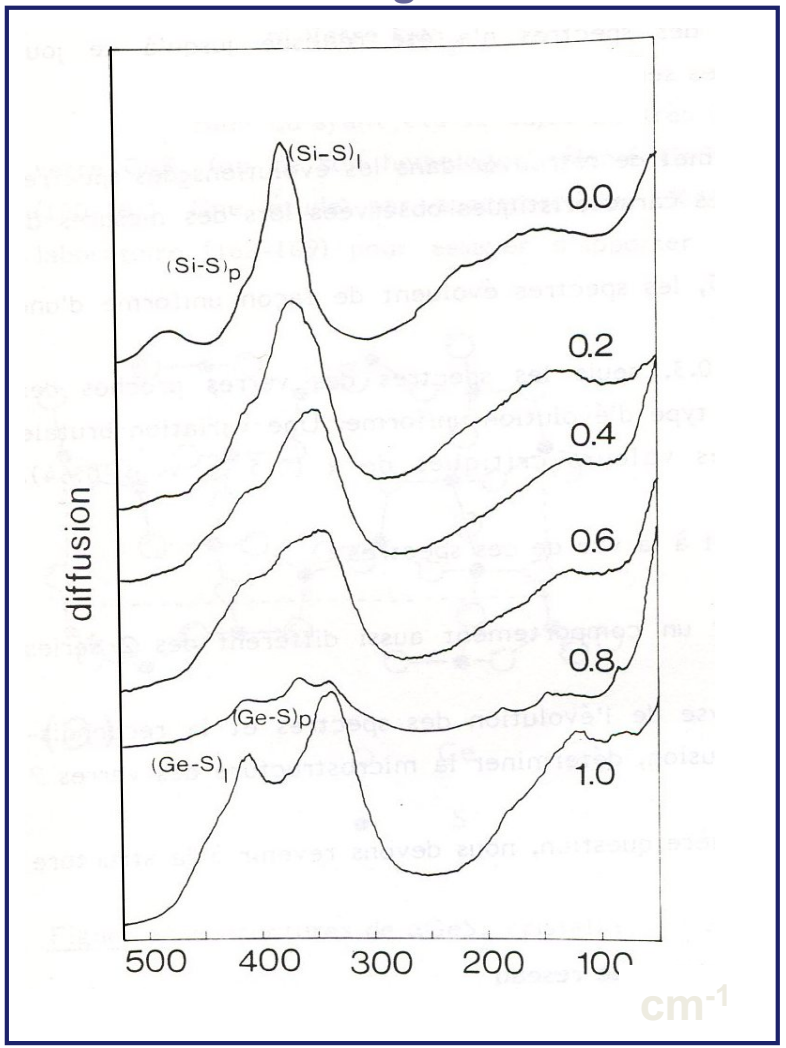
$0.3\ Li_2S\ 0.7[(1-x)SiS_2\ xGeS_2]$

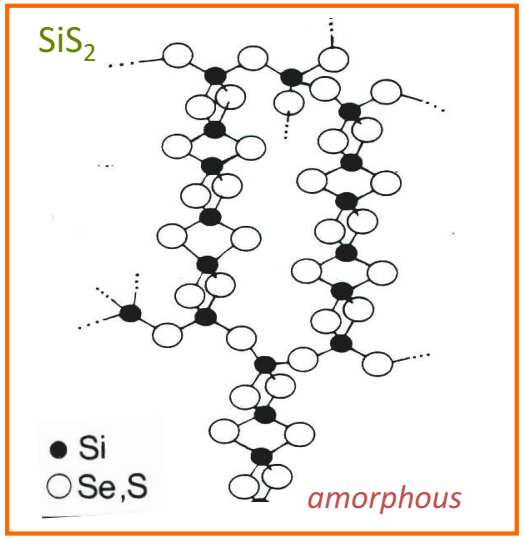
✓ A *sudden change* in the structure



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

✓ A *smooth change* in the structure

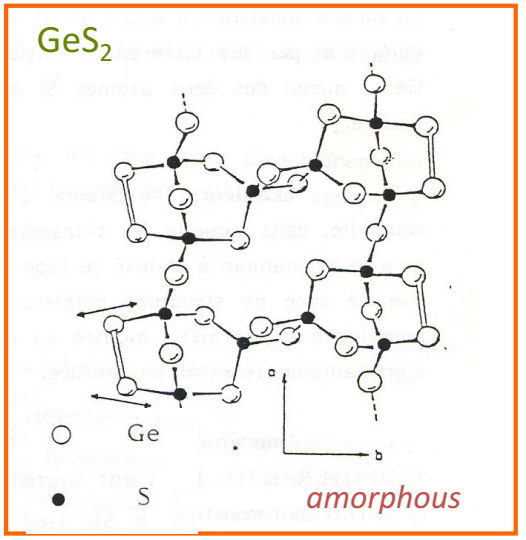




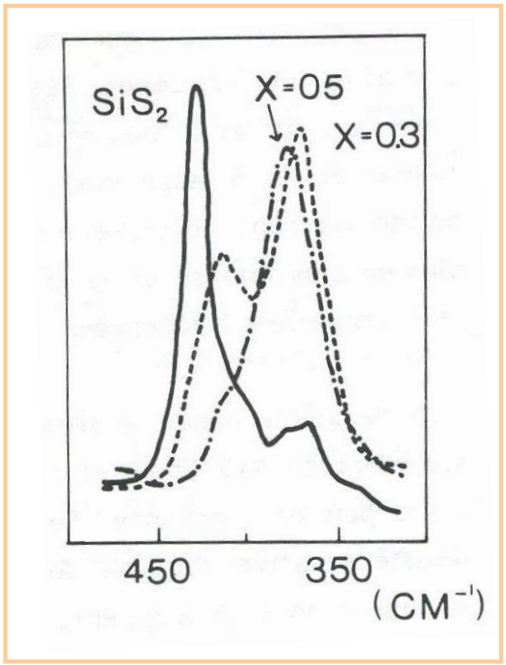
Different
medium range order

No possible mixing of the two formers

Complete phase
Separation
(Tenhover 1983)



xLi_2S- $(1-x)SiS_2$



Addition of Li_2S

↓

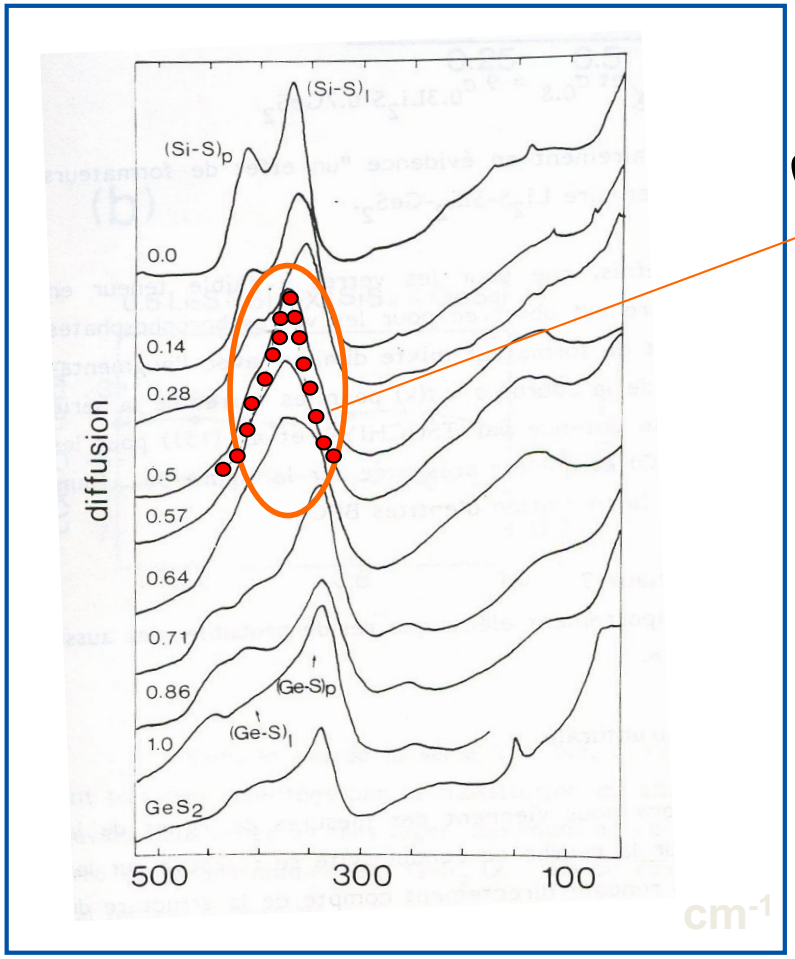
Preferential destruction
of edge sharing tetrahedra
(^{29}Si NMR investigation)

x=0.3 different MRO
phase separation

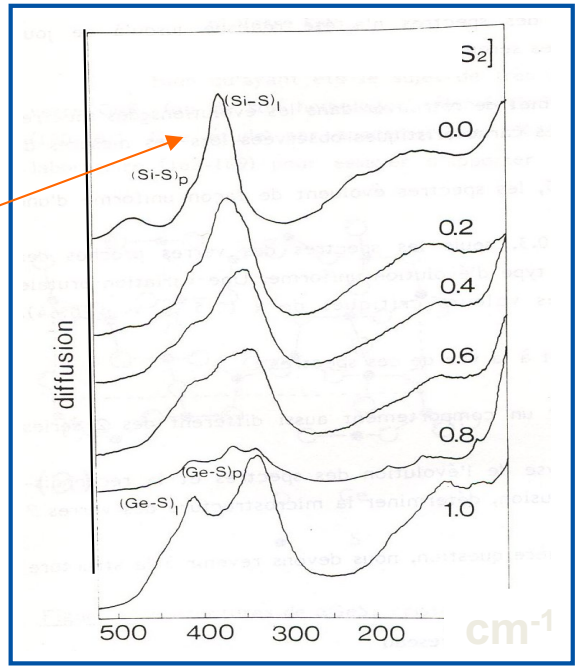
x=0.5 similar MRO
Complete solid solution

Mixed glass former effect

Raman Spectroscopy



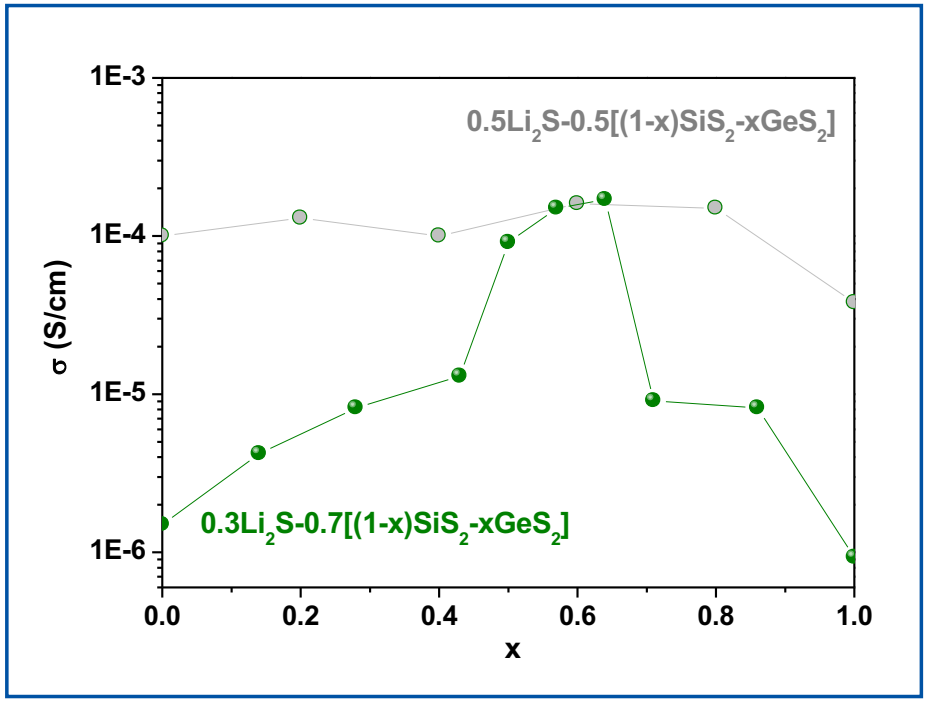
$0.5Li_2S$-
$0.5SiS_2$



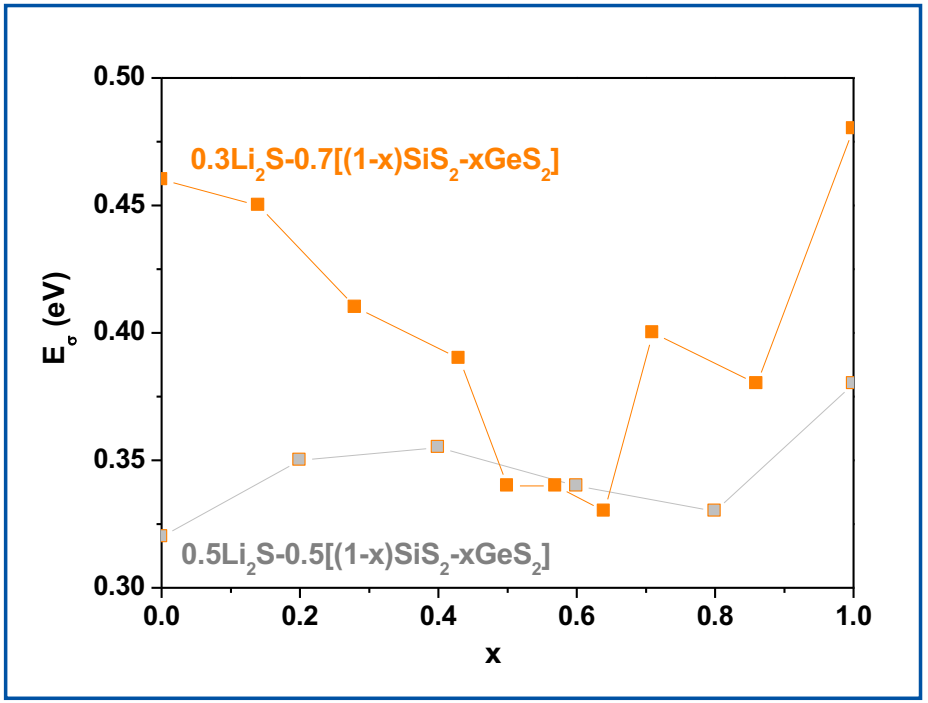
- **x = 0.5**
  0.3 [$0.5Li_2S$-$0.5SiS_2$]+ [$0.05SiS_2$-$0.35GeS_2$]
- **x = 0.57**
  0.3 [$0.5Li_2S$-$0.5SiS_2$]+ $0.4GeS_2$
- **x = 0.64**
  0.5 [$0.5Li_2S$-$0.5SiS_2$]+ [$0.05\ Li_2S$-$0.45GeS_2$]

Mixed glass former effect

Conductivity



Activation Energy



σ (phase separated glasses) ~ σ (0.5Li2S- 0.5[(1-x)SiS2-xGeS2])

E_σ (phase separated glasses) ~ E_σ (0.5Li2S-0.5[(1-x)SiS2-xGeS2])

Mixed Glass former effect

To summarize

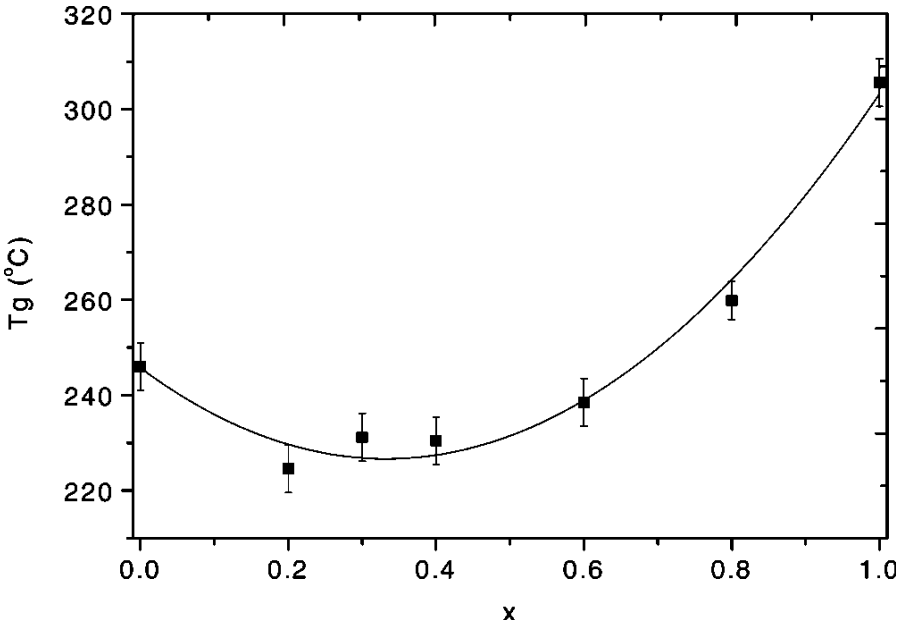
Similar structure for the formers → homogeneous mixing

Dissimilar structure for the formers → heterogeneous mixing

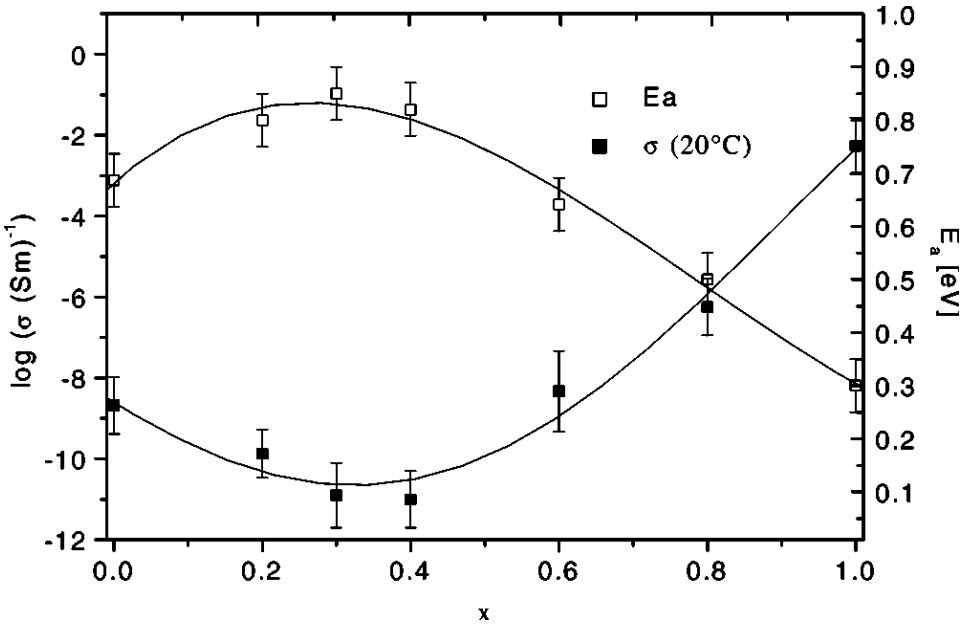
Strong consequence on both thermal and electrical properties

Mixed anion effect System $0.5[(1-x)Rb_2S\text{-}xAg_2S]\text{-}0.5GeS_2$

Vitreous transition temperature



Conductivity and Activation Energy



Non-linear variation of several physicochemical properties

Minimum in T_g and σ and maximum in E_σ

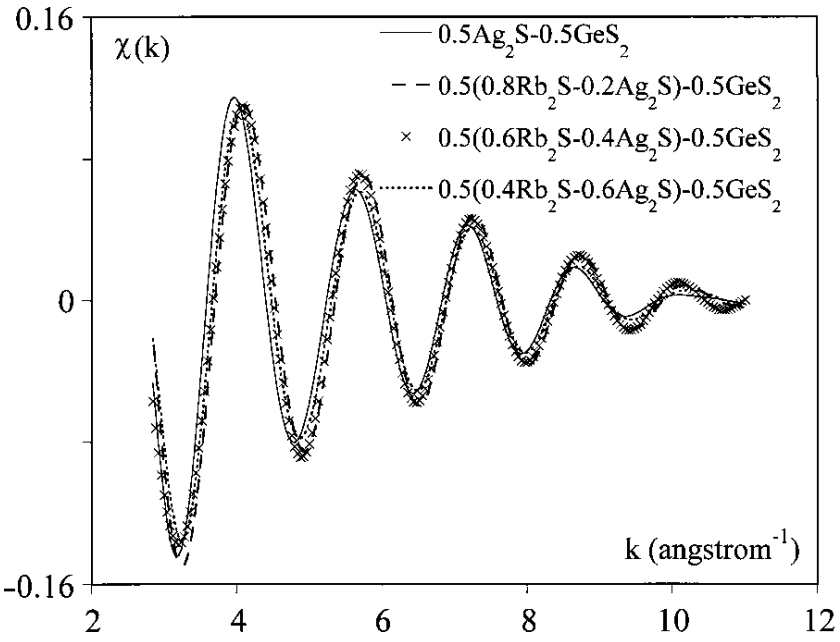
Well known « mixed alkali effect » systematically observed
when two mobile ions are mixed in a glassy matrix whatever the atoms involved
Hardly studied in chalcogenide glasses

Mixed anion effect System $0.5[(1-x)Rb_2S\text{-}xAg_2S]\text{-}0.5GeS_2$

SAXS investigation discarded the existence of any **phase separation** at a mesoscopic scale (10-1000 Å)

Structural investigation of the cation environment

Ag K-edge EXAFS (35K)



Ag *K*-edge Fourier filtered oscillations of 0.5 $[1\text{-}x)Rb_2S\text{-}xAg_2S]\text{-}0.5GeS_2$ glasses.

x	0.2	0.4	0.6	1
$N_{Ag\text{-}S}$	2.7±0.2	2.8±0.1	2.8±0.2	2.8±0.1
$\Delta\sigma$ (Å)	0.07±0.01	0.07±0.01	0.08±0.01	0.08±0.01
R (Å)	2.50±0.01	2.51±0.01	2.50±0.01	2.51±0.01
ΔE_0 (eV)	1.1±0.2	1.4±0.2	0.9±0.2	0.9±0.1

For all compositions
Coordination number $N_{Ag} \sim 2.8$
Bond length Ag-S ~ 2.50 Å

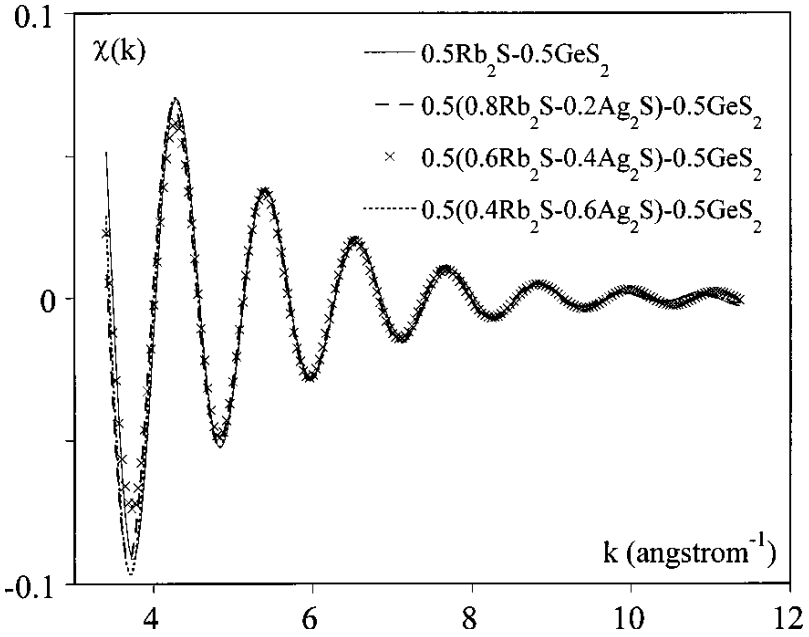
$\Delta\sigma$ = 0.08Å (disordered environment)

No influence of the presence of Rb

Mixed anion effect System $0.5[(1-x)Rb_2S\text{-}xAg_2S]\text{-}0.5GeS_2$

Structural investigation of the cation environment

Rb K-edge EXAFS measured at 35K



Rb *K*-edge Fourier filtered oscillations of 0.5 $[1\text{-}x)Rb_2S\text{-}xAg_2S]\text{-}0.5GeS_2$ glasses.

x	0	0.2	0.4	0.6
$N_{Rb\text{-}S}$	4.2±0.2	4.2±0.2	4.1±0.2	4.3±0.2
$\Delta\sigma$ (Å)	0.14±0.01	0.14±0.01	0.14±0.01	0.13±0.01
R (Å)	3.37±0.01	3.37±0.01	3.37±0.01	3.38±0.01
ΔE_0 (eV)	1.6±0.3	0.9±0.3	1.4±0.3	1.2±0.2

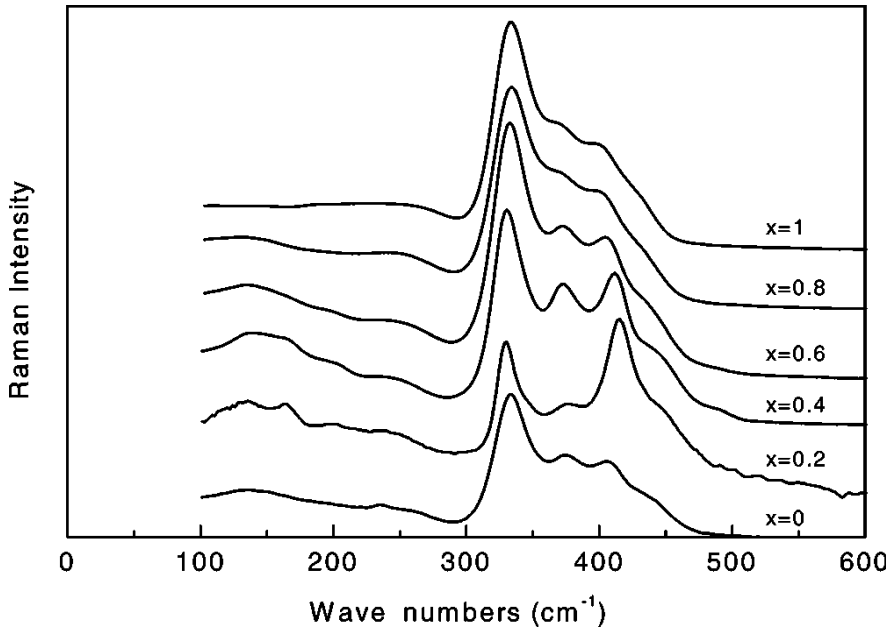
For all compositions
Coordination number N_{Rb} ~ 4 (Td)
Bond length Rb-S ~ 3.37 Å
$\Delta\sigma$ = 0.14Å (highly distorted sites)

No influence of the presence of Ag

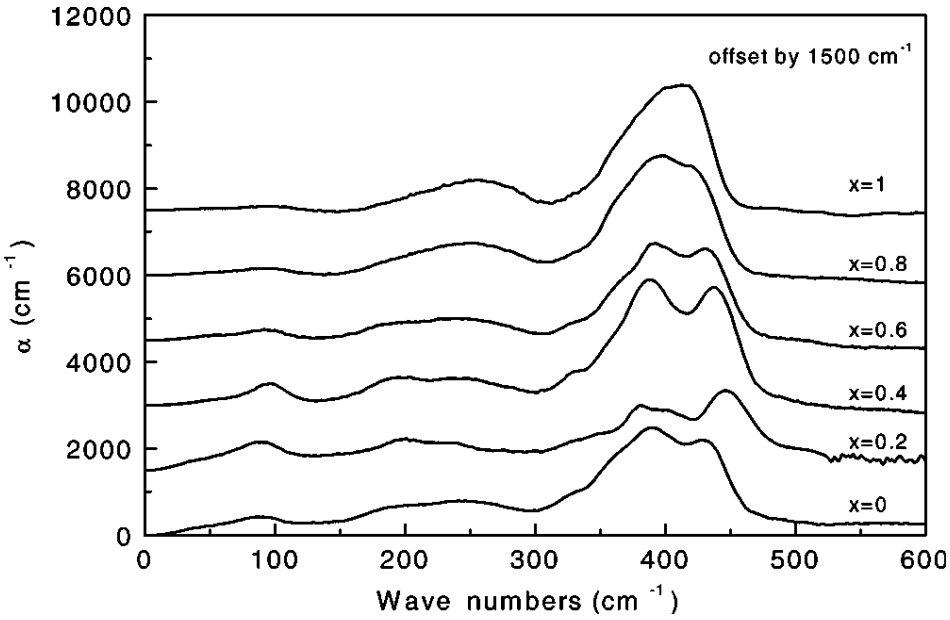
Mixed anion effect System $0.5[(1-x)Rb_2S\text{-}xAg_2S]\text{-}0.5GeS_2$

Structural investigation of the glassy network

Raman (1064 nm)



IR spectra



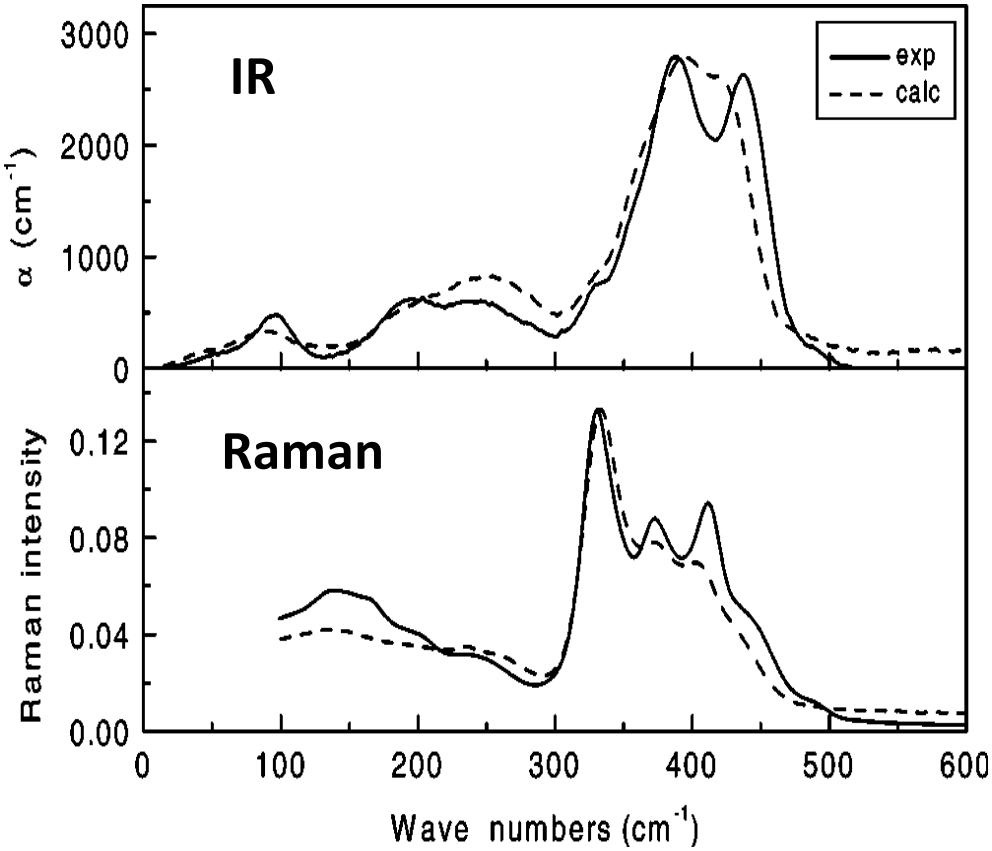
Clear structural rearrangements upon gradual replacement of Rb_2S by Ag_2S.

Nonmonotonic evolution - strong departure for x = 0.2 and 0.4

Mixed anion effect System $0.5[(1-x)Rb_2S\text{-}xAg_2S]\text{-}0.5GeS_2$

Structural investigation of the glassy network

X = 0.4



Linear combinations of the end-member spectra (*x*=0 and 1)

Experimental spectra

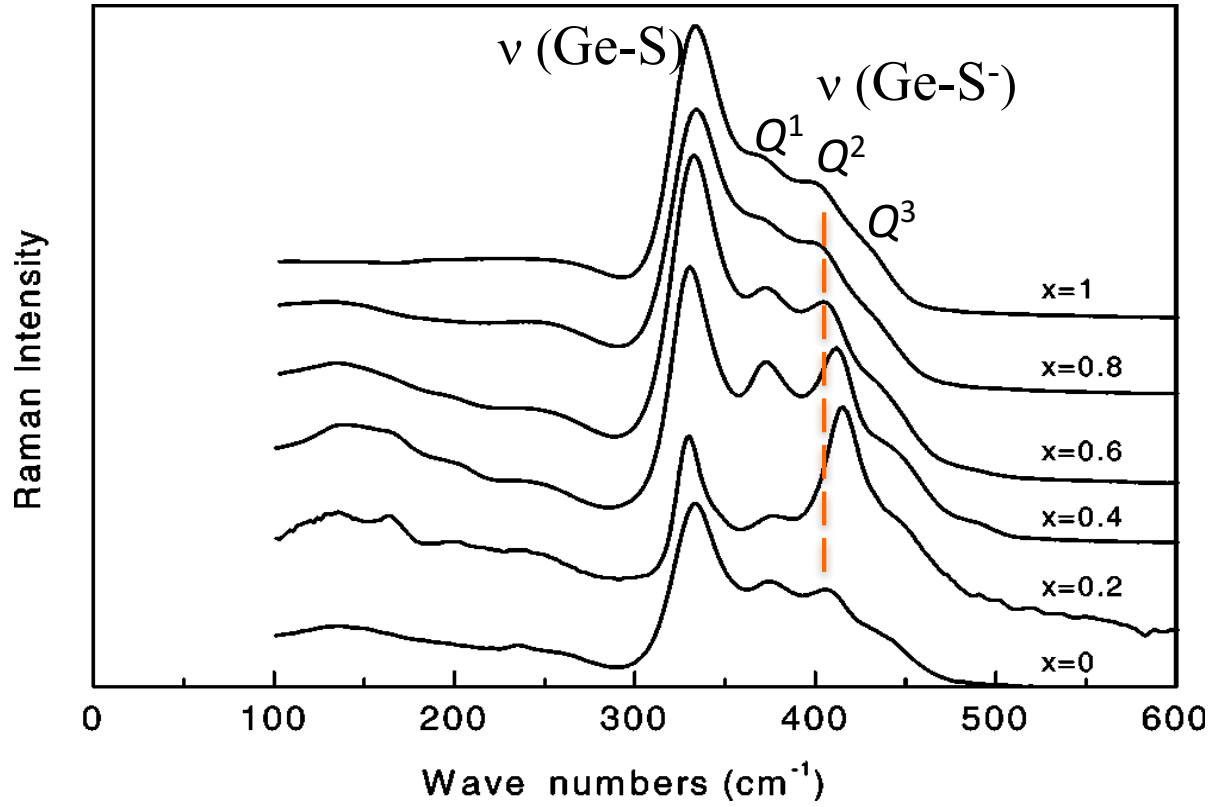
A simple linear mixing of the structures of the two end-member glasses cannot reproduce the thiogermanate structure of the cation-mixed glass.

Mixed anion effect System $0.5[(1-x)Rb_2S\text{-}xAg_2S]\text{-}0.5GeS_2$

Structural investigation of the glassy network

$3\ Q^2 \rightarrow Q^4 + 2Q^1$

$2\ Q^2 \rightarrow Q^3 + Q^1$



Shift of ν (Ge-S⁻) of Q^2 Td units to higher frequency → local strain effects

Increase in Q^2 units for x= 0.2 and 0.4 → a more homogeneous glass structure and a more uniform distribution of anionic sites hosting the Rb^+ and Ag^+ cations

Mixed Anion Effect

To summarize

The environment of the cations is not affected by the presence of another cation in the network

The network relaxes to adjust to maximize the distance between dissimilar cations creating a more homogeneous matrix

Strong consequence on both thermal and electrical properties

Conclusions

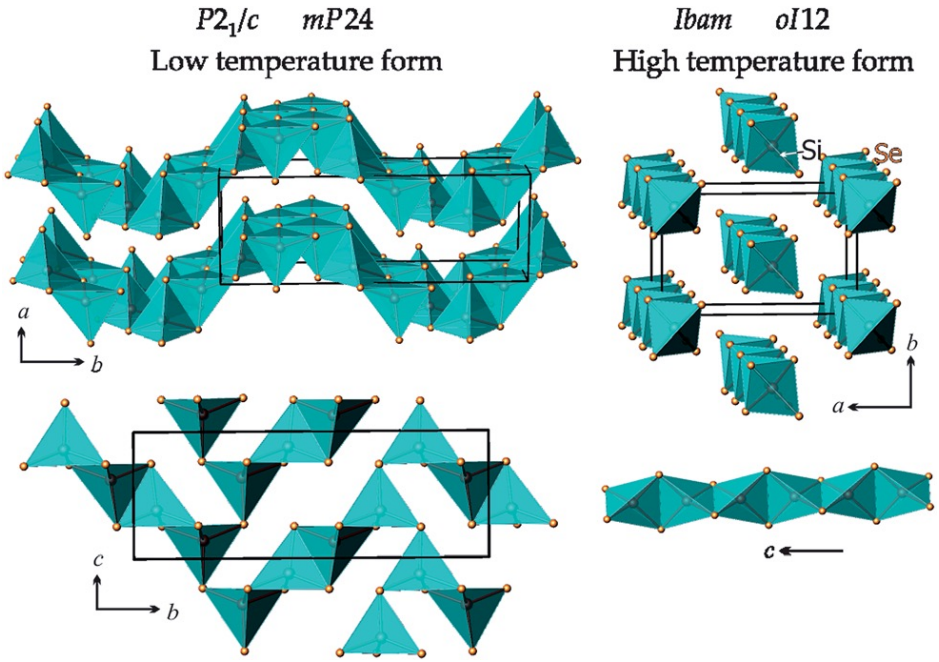
Chalcogenide glasses different from oxide glasses

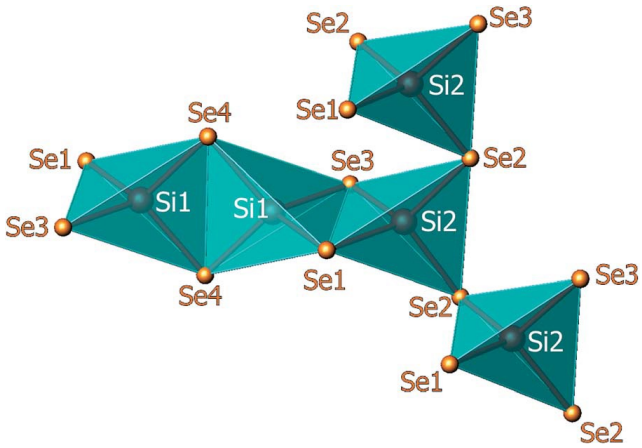
Presence of edge-sharing Td

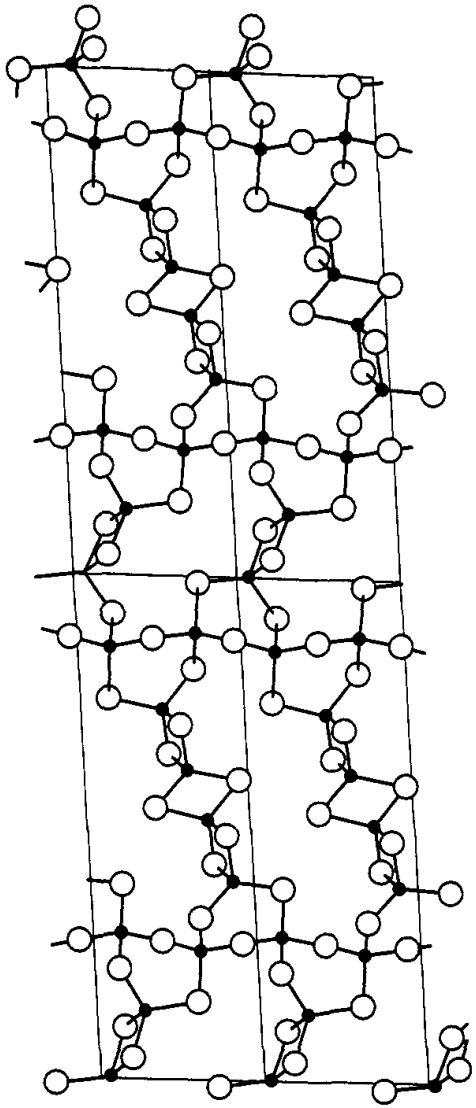
But also many similarities

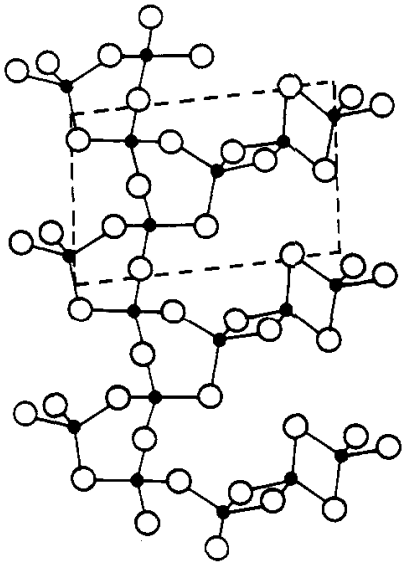
Bridging vs non-bridging chalcogens
Mixed glass former effect
Mixed alkali effect

THANK YOU !


$P2_1/c$ $mP24$
Low temperature form
$Ibam$ $oI12$
High temperature form
Si
Se
a
b
c
b
a
c
b


Se2
Se3
Si2
Se1
Se4
Se1
Si1
Si1
Se3
Se2
Se3
Si2
Se4
Se1
Se2
Se3
Si2
Se1
Se2



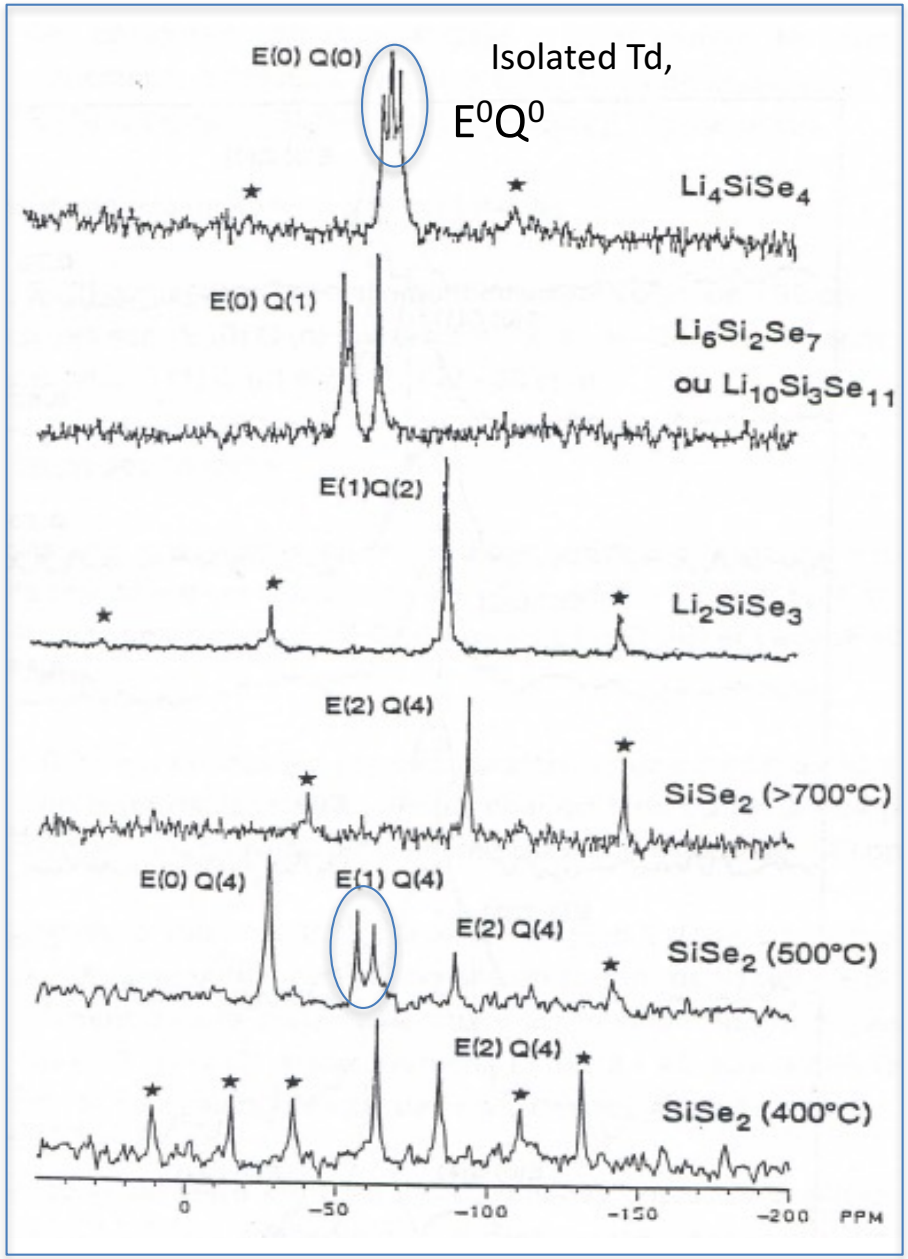


Role of modifier on the structure

Modified chalcogenide glasses

Investigation of crystalline phases in the system $xLi_2Se-(1-x)SiSe_2$

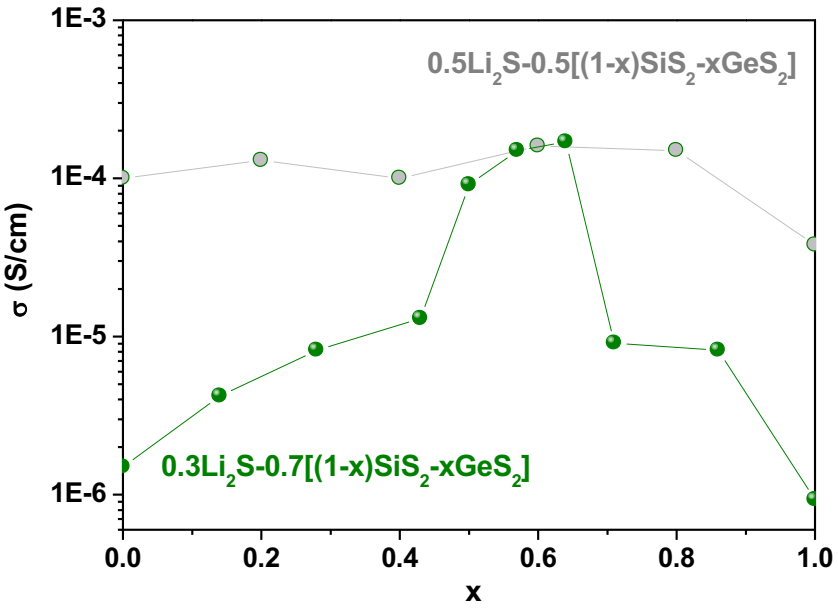
No apparent chemical shift between E^nQ^4 units and E^nQ^2 units



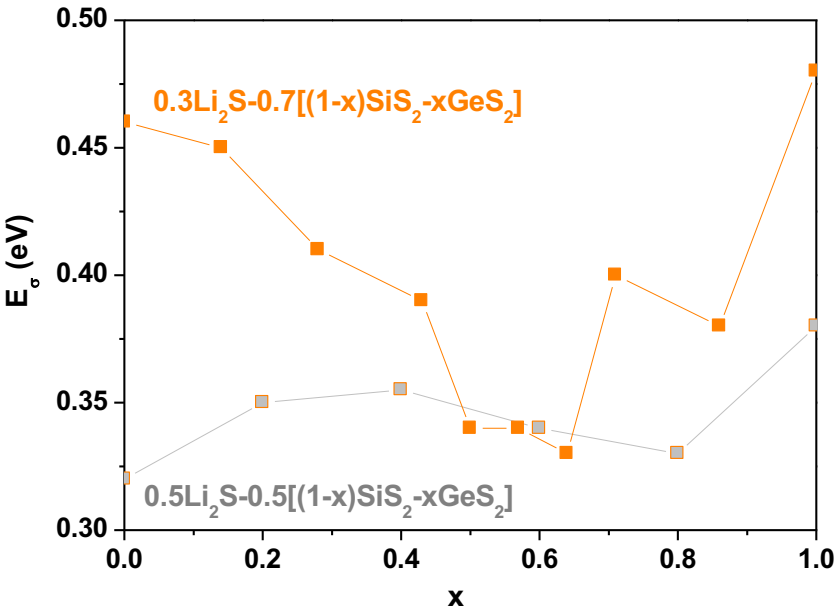
System Li_2S- $[(1-x)SiS_2$-$xGeS_2]$:: Conductivity and E_σ

Mixed glass former effect: Chalcogenide glasses

Conductivity



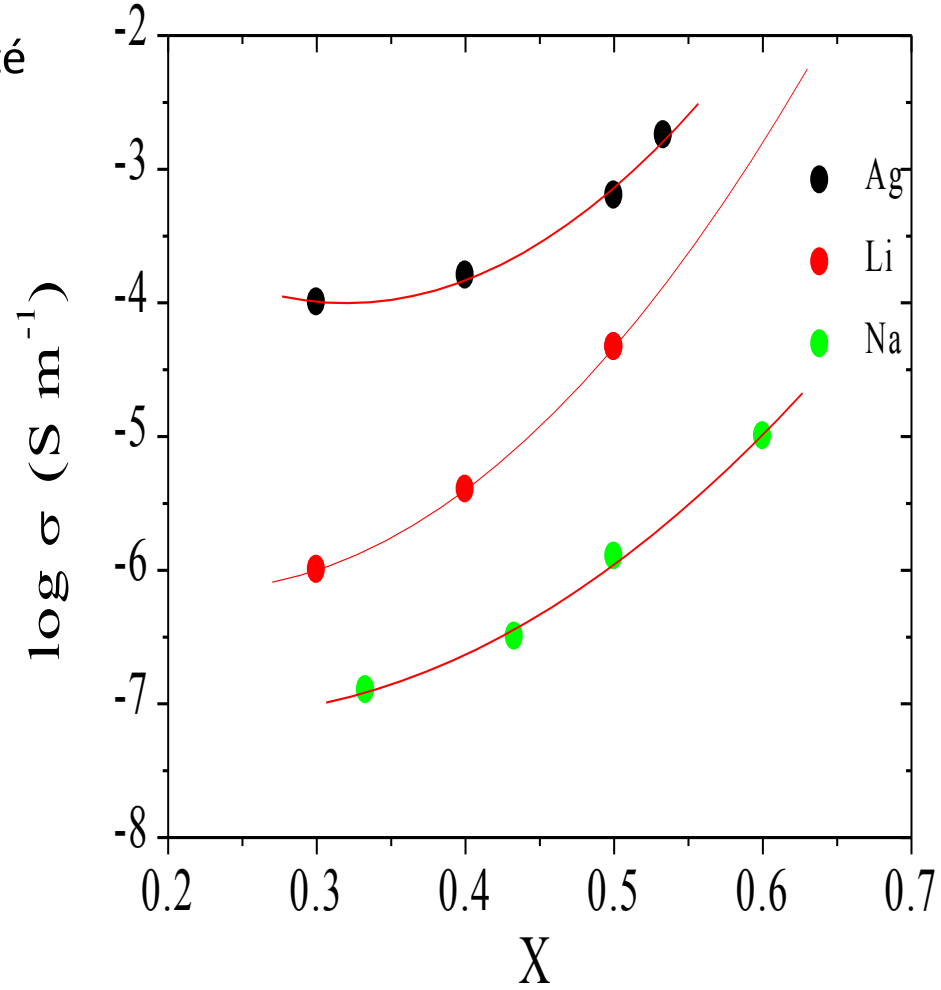
Activation energy



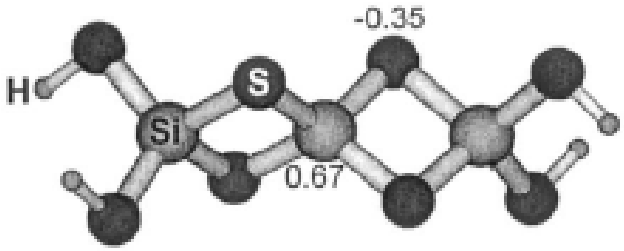
Modified chalcogenide glasses **Role of modifier on the structure**

Role of alkali (silver) on the structure

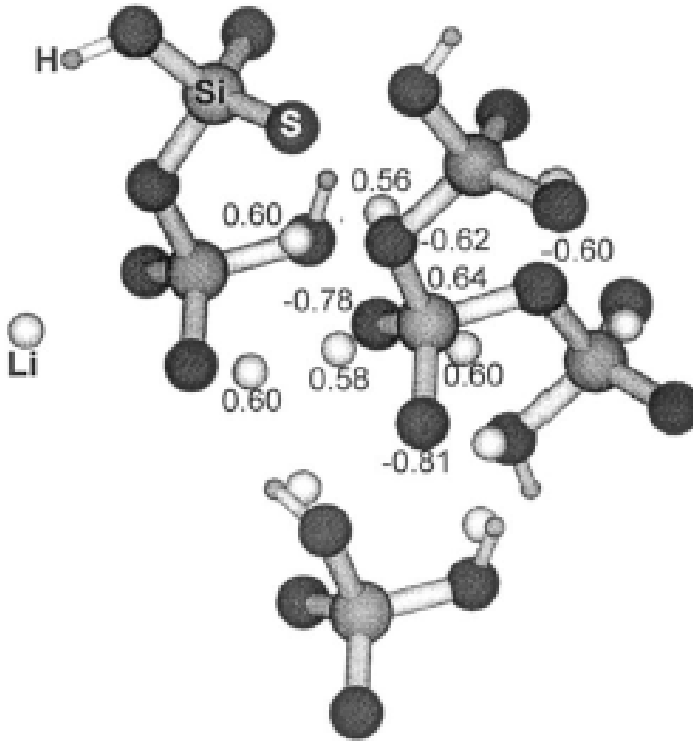
Propriétés : Tg conductivité



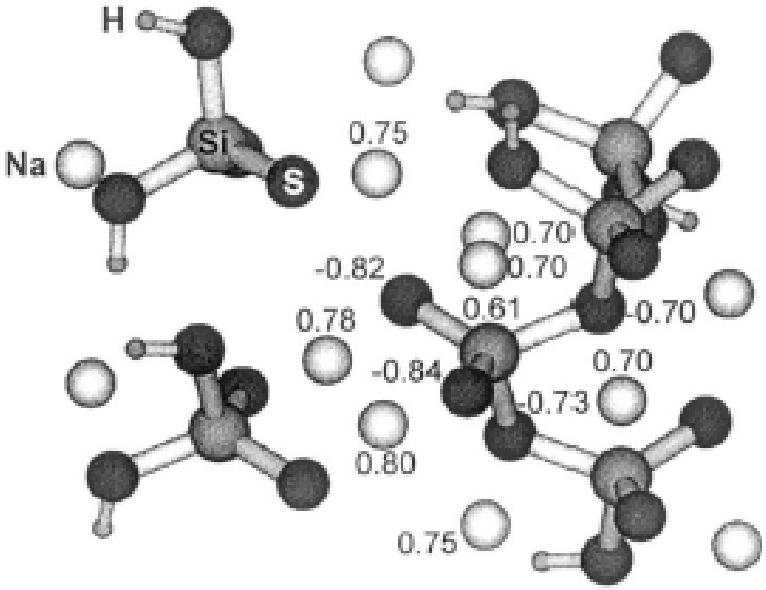
SiS_2



Li_2SiS_3



Na_2SiS_3

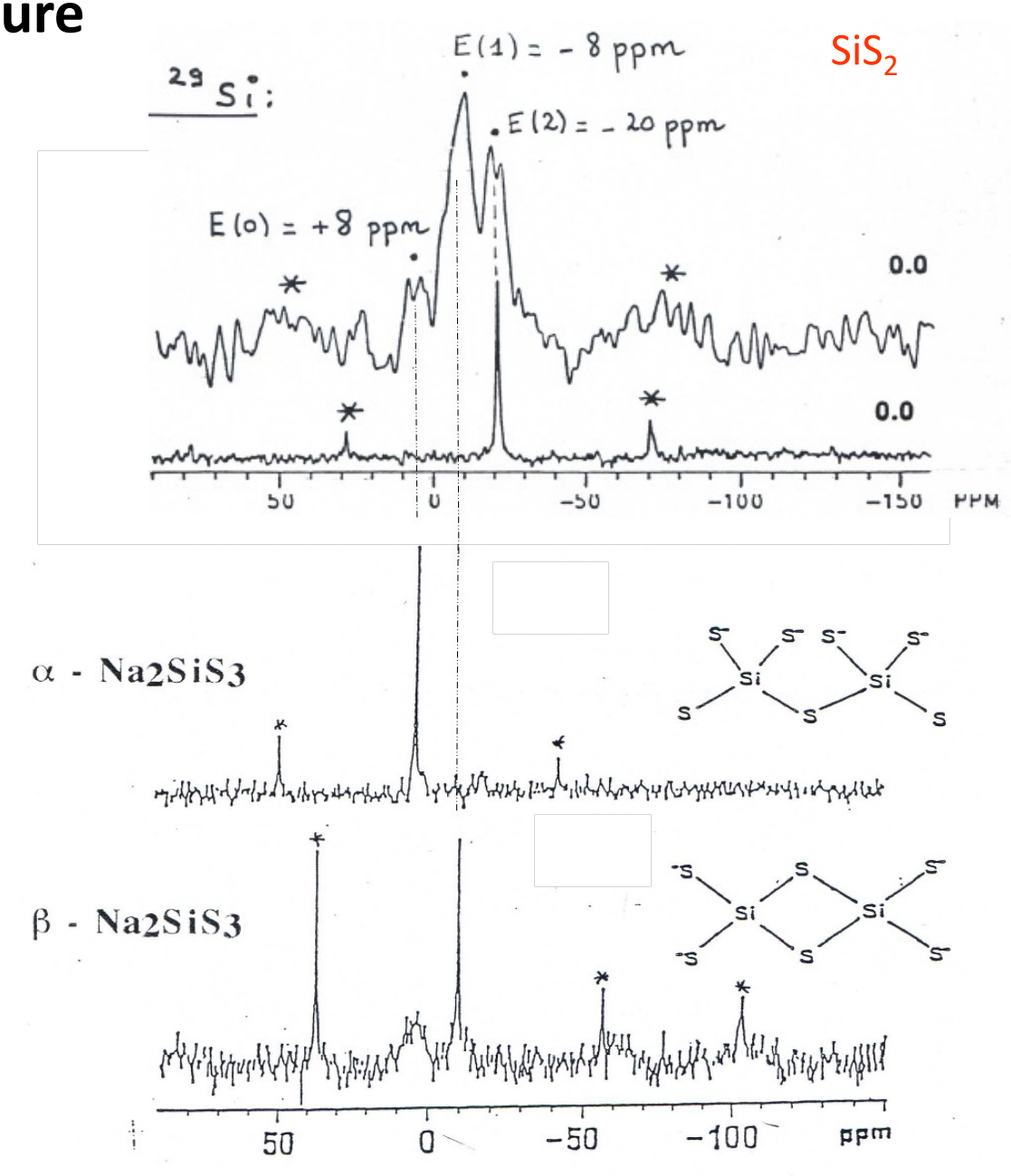


Role of modifier on the structure

Crystalline compounds

System xNa_2S- $(1-x)SiS_2$

X = 0.5



No apparent chemical shift between E^nQ^4 units and E^nQ^2 units