Fragility of High BaO Containing Glasses

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- Compositions Investigated
- Structural Descriptions
- **Viscosity and Fragility**
- Invert Glass Hypothesis
- Results and Discussion

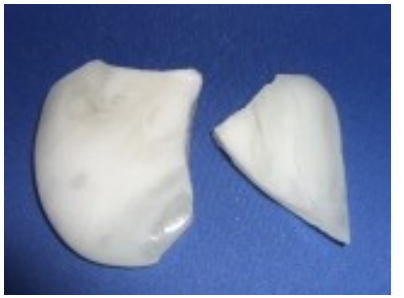
Sample composition and occurrence

Sample/ mol%	BaO	SiO_2	B_2O_3	$(Zr,Hf)O_2$	La_2O_3
48	**48**	**37**	5	5	2,5
45	**45**	**40**	5	5	2,5
40	**40**	**45**	5	5	2,5
35	**35**	**50**	5	5	2,5
25	**25**	**60**	5	5	2,5
15	**15**	**70**	5	5	2,5

→ crystalline

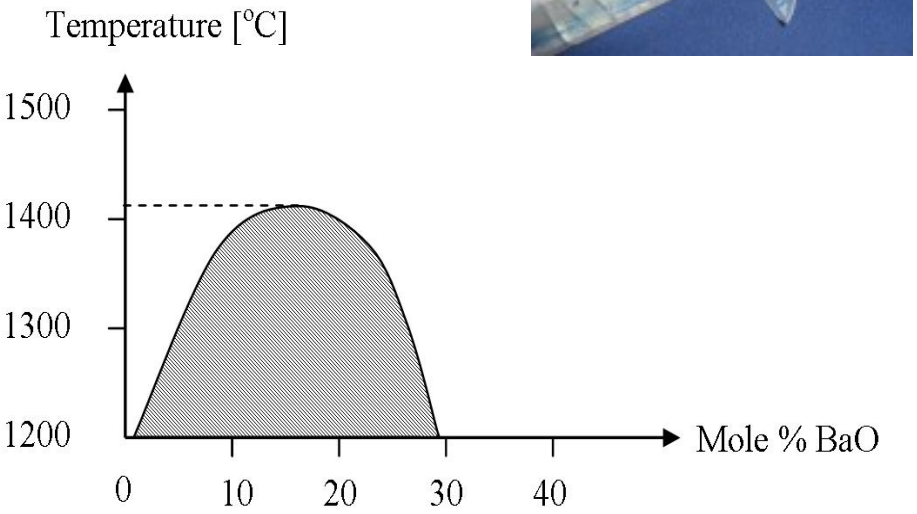
→ glassy

→ l/l phase separated

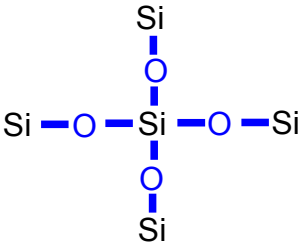


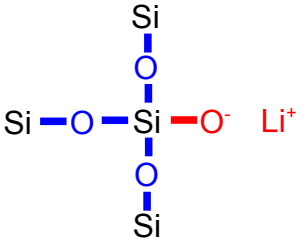
- Melting procedure:
  1500°C, 2h
- cast in C mould
- annealed at 690°C

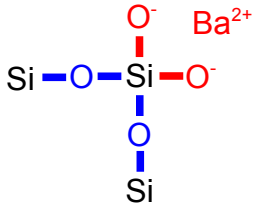
48: crystalline at any casting conditions
25: cloudy in the middle
15: entire sample is phase separated

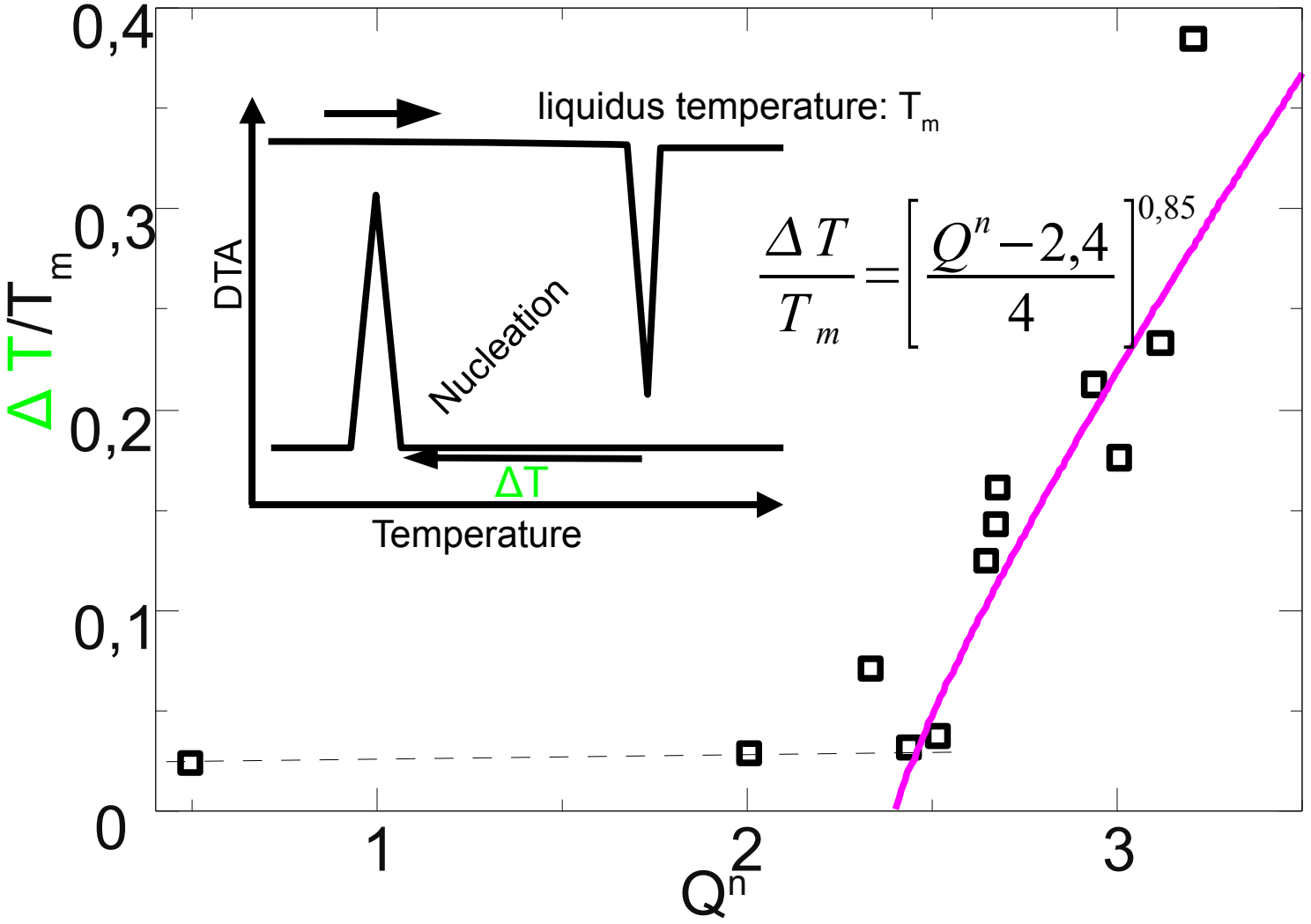


Prediction of glass forming from the composition

$Q^n=4$: 

$Q^n=3$: 

$Q^n=2$: 



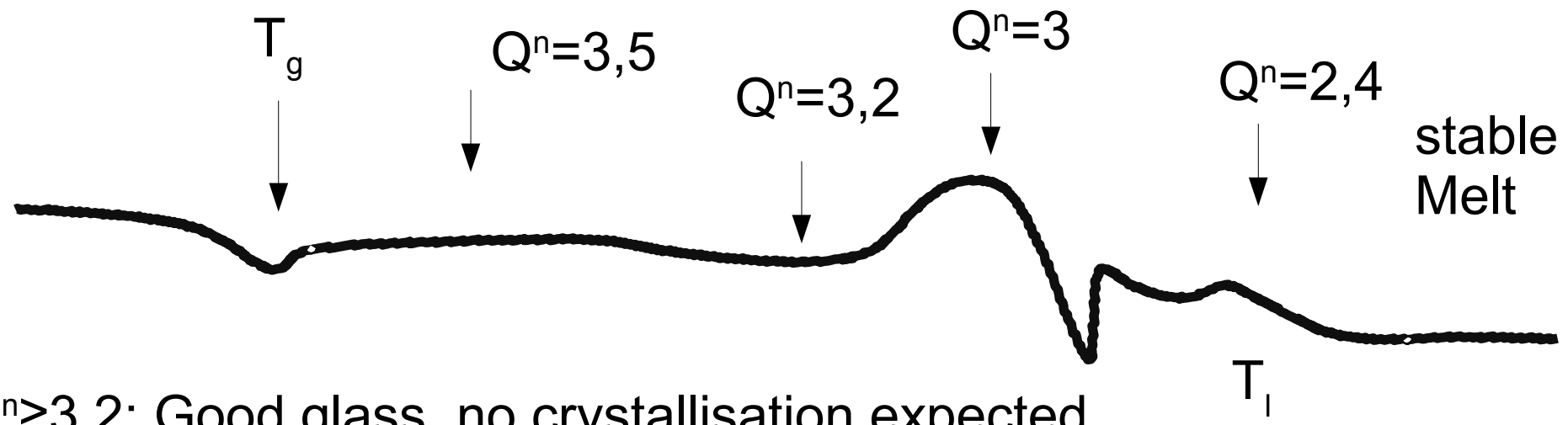
More network former
higher undercooling
better glass formability

Quantified from the composition

Separation between
Network former NF
and
Network modifier NM

Assumption:
statistic distribution of
NF and NM

Stable glasses and Q_n



$Q^n \geq 3,2$: Good glass, no crystallisation expected
$Q^n = 3,0$: Surface crystallisation, glasses for nucleation experiments
$Q^n = 2,7$: Glass obtained by quenching on Cu-blocks
$Q^n \leq 2,4$: No glass

Assuming:

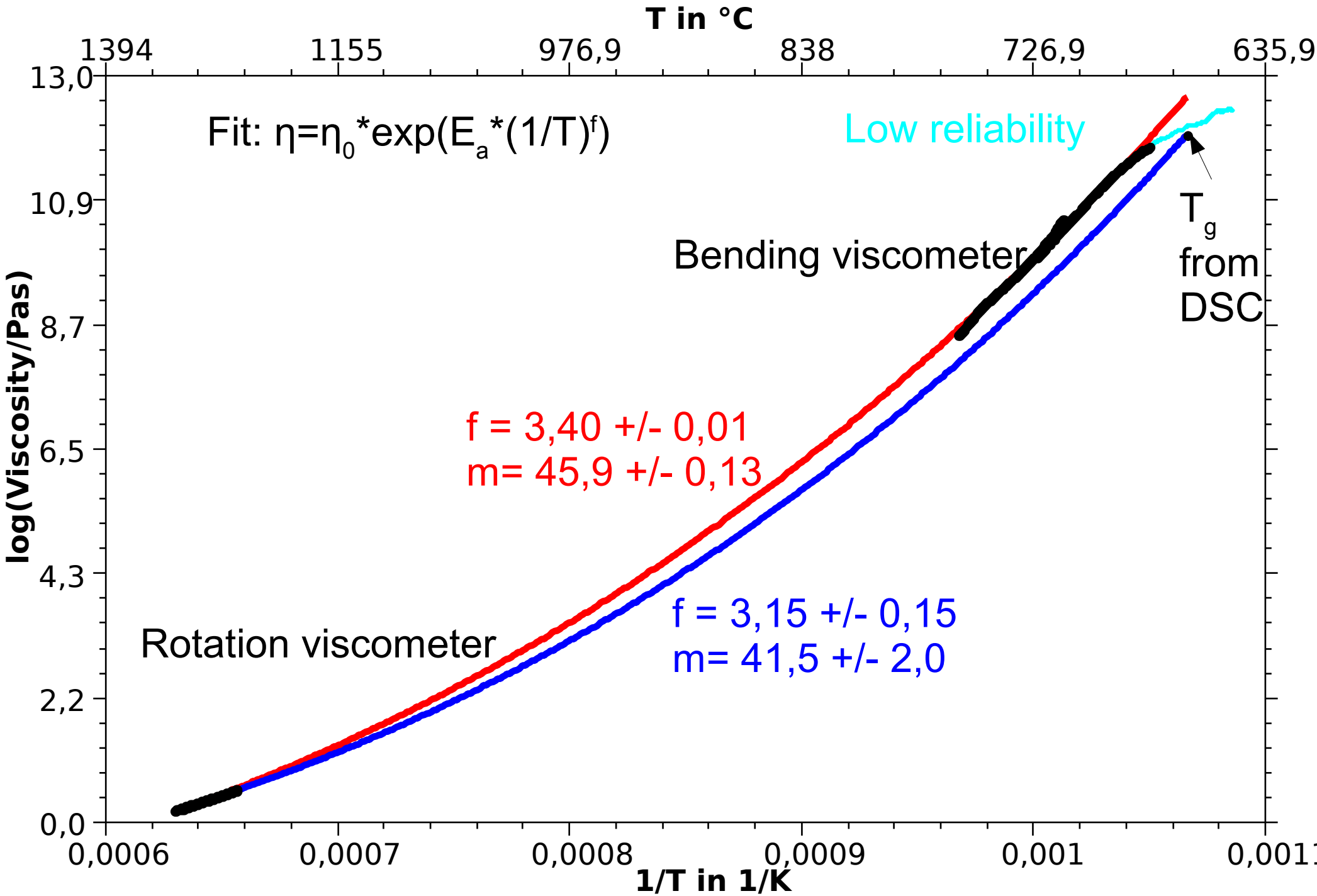
La	NM
Ba	NM
Zr	NF
Si	NF
$^{[3]}B$	NF

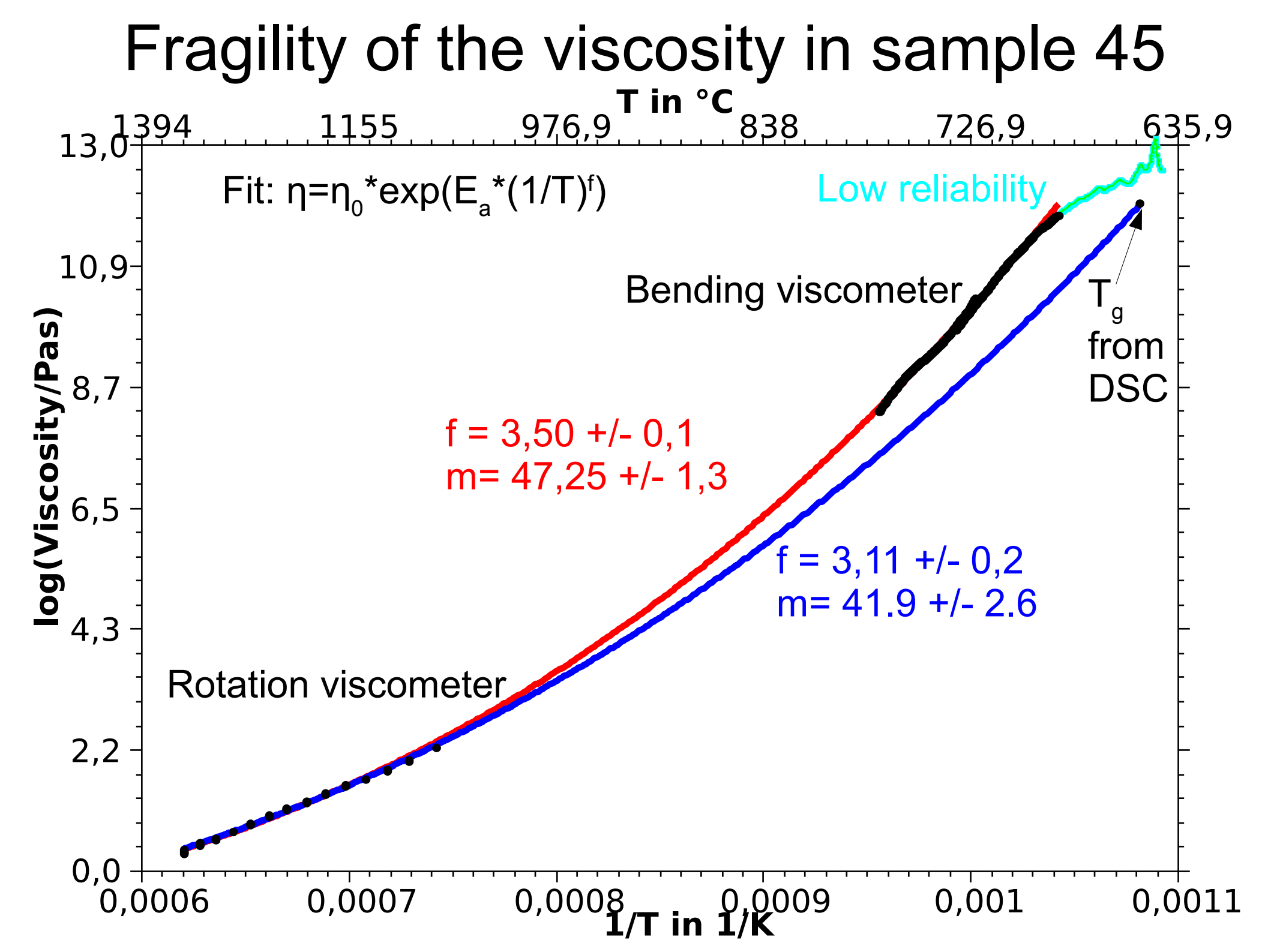
Sample	Q^n
48	1,67
45	1,91
40	2,25
35	2,54
25	3,00
15	3,35

The stability of the melts 45,40 and 35 against crystallisation are in contradiction to Q_n and are quite unique.

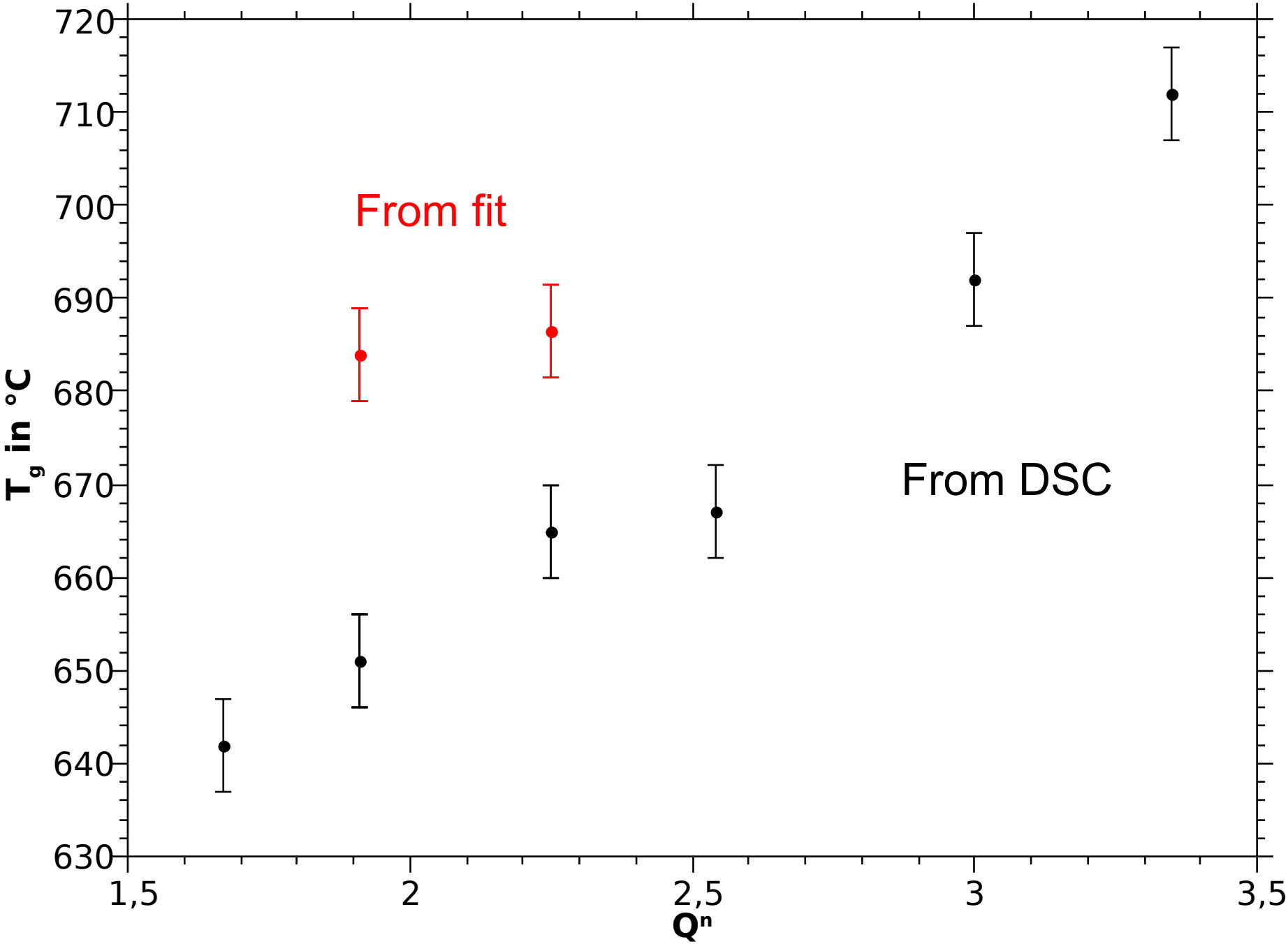
Is the theory wrong?

Fragility of the viscosity in sample 40

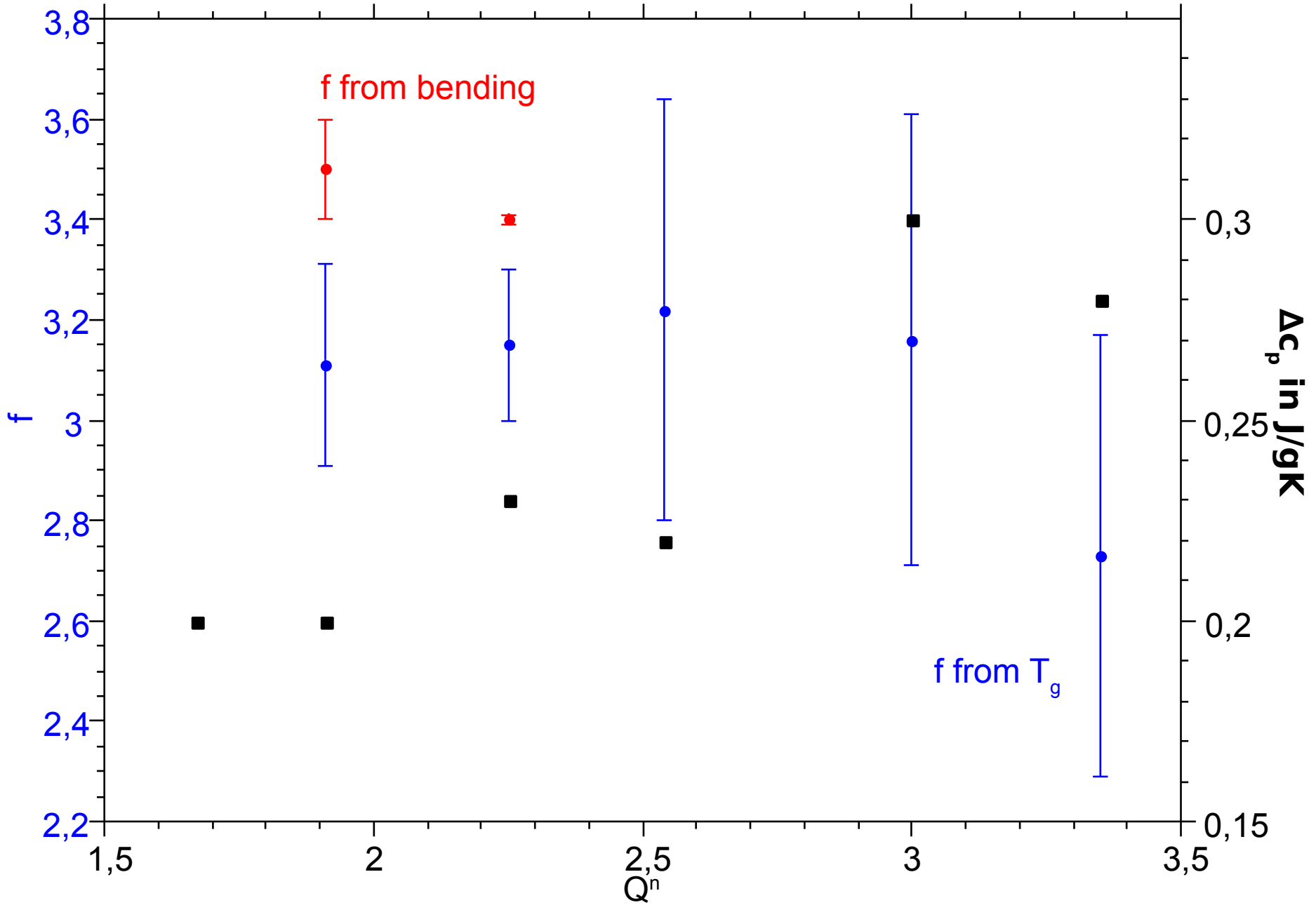



Fragility of the viscosity in sample 45
T in °C
1394
1155
976,9
838
726,9
635,9
13,0
10,9
8,7
6,5
4,3
2,2
0,0
log(Viscosity/Pas)
Fit: η=η0*exp(Ea*(1/T)f)
Low reliability
Bending viscometer
Tg from DSC
f = 3,50 +/- 0,1
m= 47,25 +/- 1,3
f = 3,11 +/- 0,2
m= 41.9 +/- 2.6
Rotation viscometer
0,0006
0,0007
0,0008
0,0009
0,001
0,0011
1/T in 1/K

Glass Transition Temperature T_g



Fragility and Δc_p in dependence of Q^n



Invert glass

Invert Glass: has less than 50% network former

Literature:

15 Na_2O, 15 K_2O, 15 CaO, 15 BaO, 40 SiO_2 (Stevels, Trapp 1959):
crystallises even on Cu-plate quenching

11-32 Na_2O, 21-37 CaO, 8-16 Al_2O_3, 30-42 P_2O_5 (Vogel 1992)
but: 1. Al will take 1 NM charge and
there are 2 NF in the Al_2O_3 and P_2O_5 formula

Structural explanation of the existence of invert glasses:

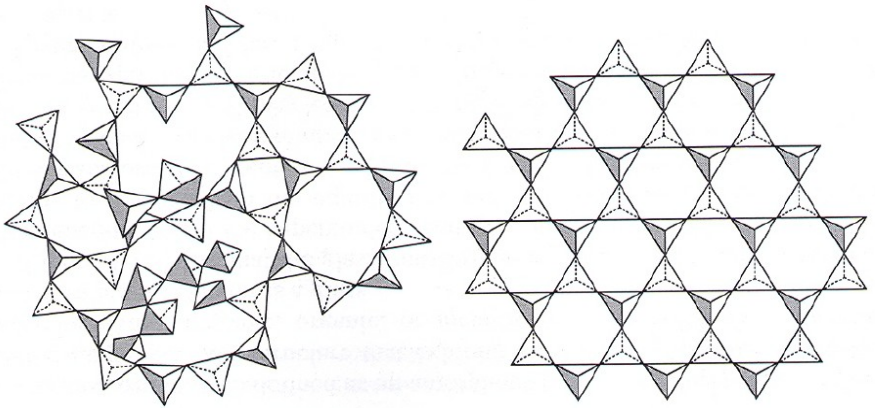
- There is chaos in the arrangement of the cations,
- Cations will need more time to rearrange to crystal than the cooling time
- **assumption of a cationic network**

In the melts here: much higher degree of depolymerisation

Structure in the investigated glass

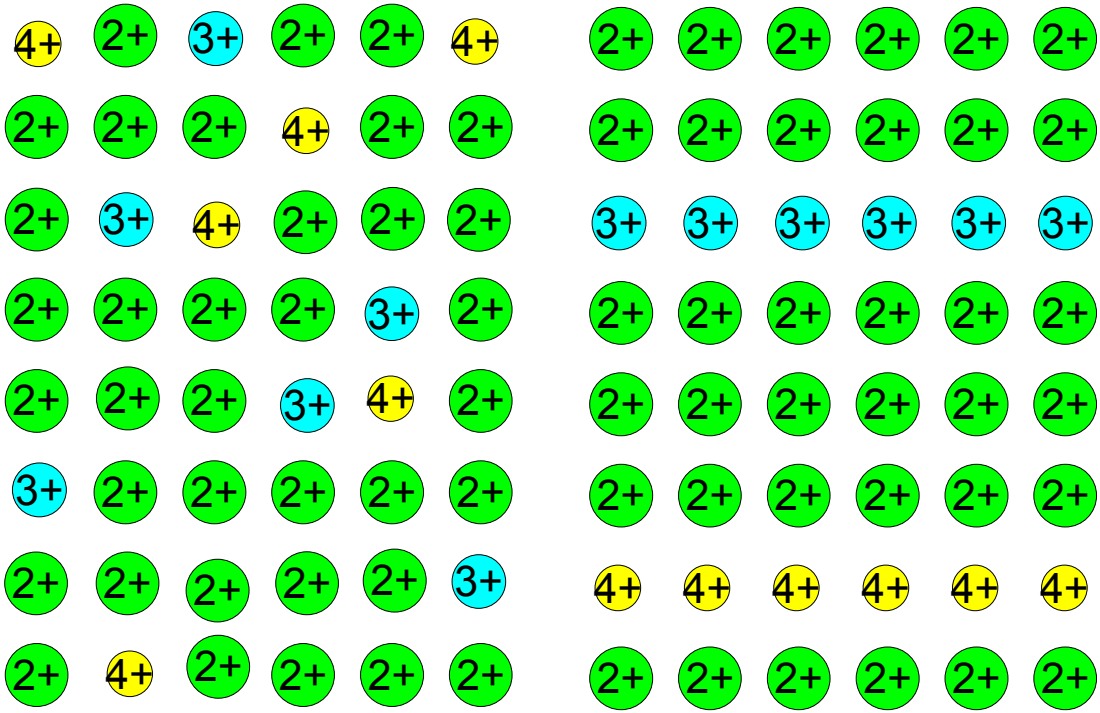
Ba^{2+}, Zr^{4+}, La^{3+} : All are large ions with different charge

Normal glass:



Conversion from liquid structure to crystalline one requires Si-O-Si bond breaking:
high activation energy
low crystallisation, nucleation
Large size of collective moving units: low fragility

Invert glass investigated:

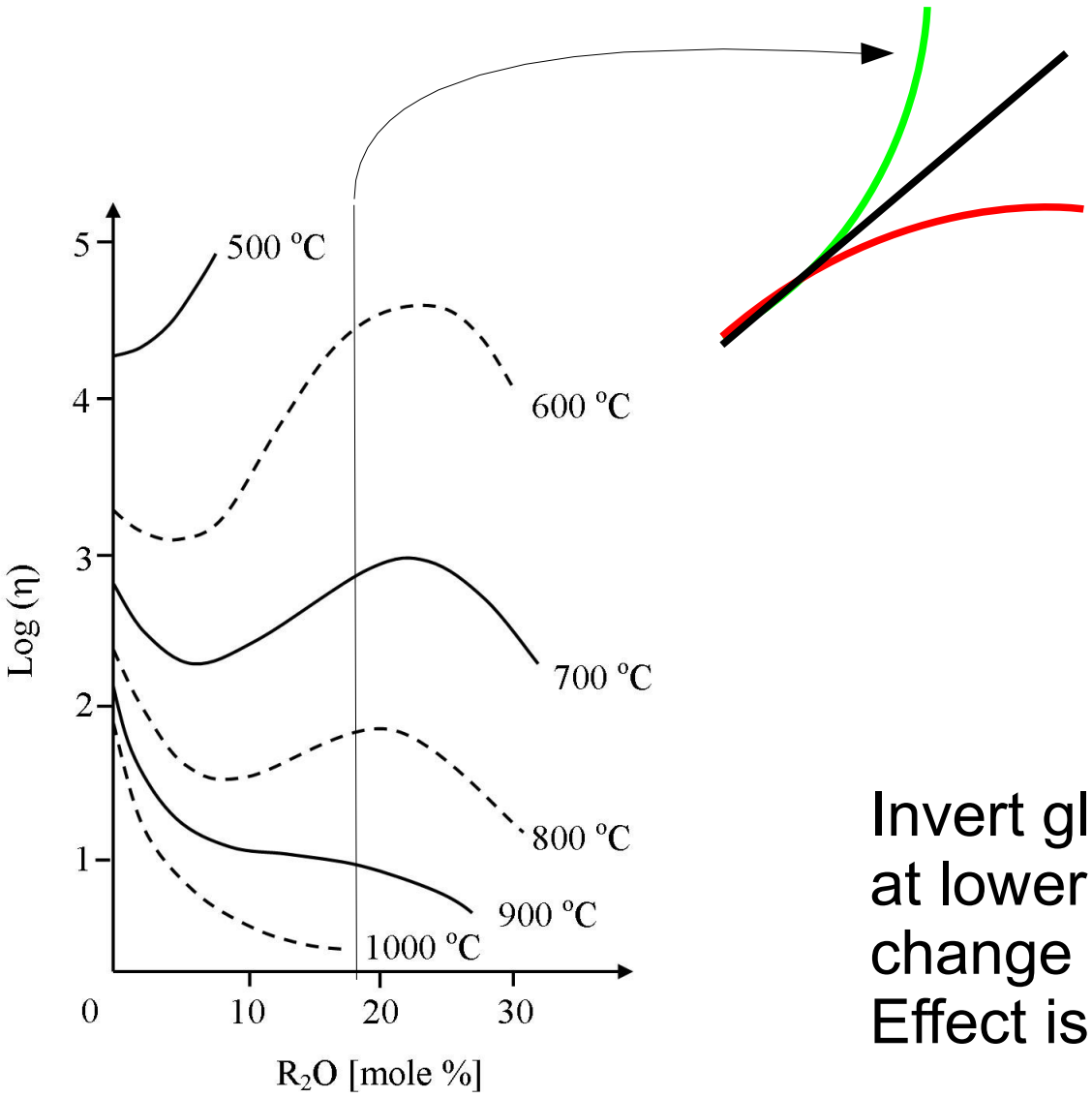


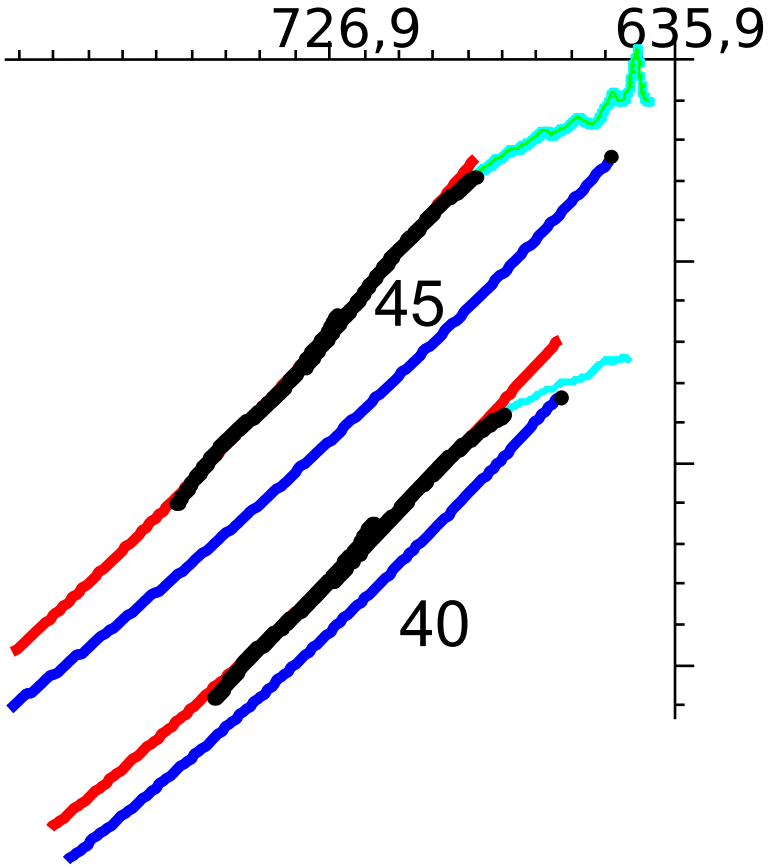
Conversion melt – crystal requires transportation over large distances:
high activation energy
Low crystallisation, nucleation
Large size of collective moving units: low fragility

Invert glass and boric acid anomaly

$^{[3]}B$ will become $^{[4]}B^-$ at lower T:

- anionic network will increase Q^n
- cationic network will lose 1 charge





Invert glasses will be **de**polymerised at lower T because of coordination change of B at low temperature.
Effect is stronger at more invert glasses

Results and conclusion

The system $xBaO\ (85-x)SiO_2\ 5B_2O_3\ 5ZrO_2\ 2{,}5La_2O_3$

- forms bulk size glasses x=15 ... 45, Q^n= 1,91 ... 3,35
- crystallizes at x=48
- liquid – liquid phase separates at x=15 and 25

The melts at x=45 and 40

- they are stabile in air
- are unusual resistant against crystallisation
- the fragility (3,5 and 3,4) is unexpected low
- the Δc_p for T_g is comparable low
- exhibits a reverse boric acid anomaly effect
  - fragility should not be calculated from T_g measured by DSC

The properties of the BaO rich melts gives hints for a cationic network. This idea can describe the observed effects. The theory is rescued.

The system could be used as a model system for high network modifier containing melts and glasses.

At higher BaO content

- the melt forms a glass
- the Δc_p is comparable low
- the f will not decrease any more
- the f is lower than expected

Generally

- changes in T_g are small
- there is a decrease for the T_g measured
  and the one extrapolated from the fragility
- the decrease is more pronounced at high BaO content

Sample	Q_n ($B^{[4]}$)	Q_n ($B^{[3]}$)
48	2.06	1.67
45	2.27	1.91
40	2.58	2.25
35	2.85	2.54
25	3.27	3.00
15	3.59	3.35