Ionic Conductivity of Lithium Borosilicate Glasses

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The SPIRIT of science

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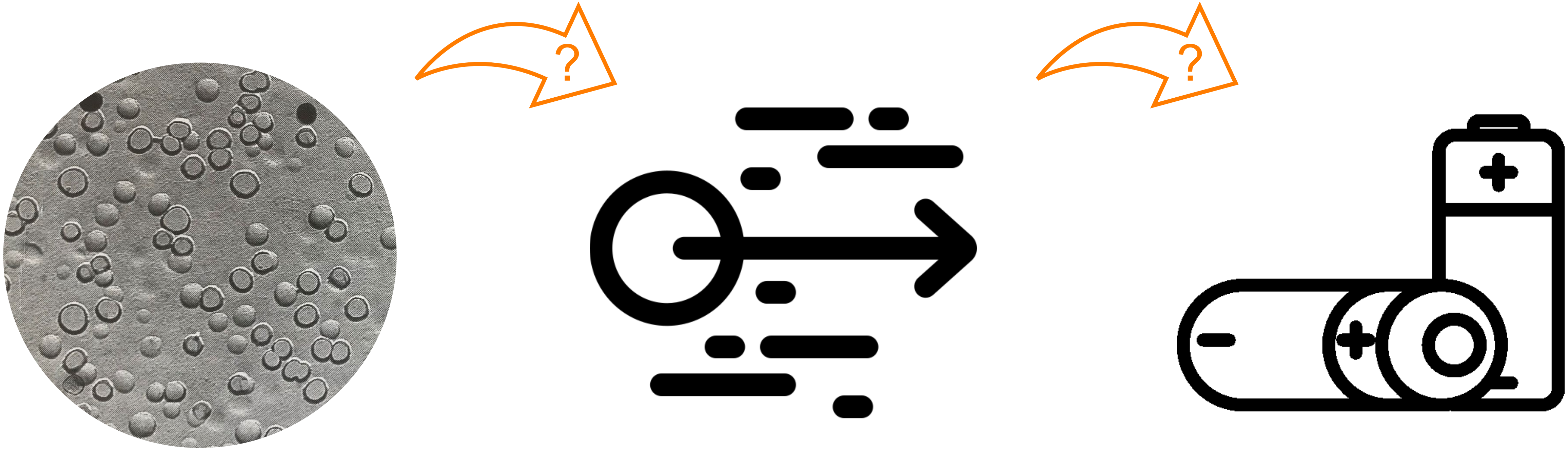
1. Aim and motivation



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Systems with increased ionic conduction by interfaces

mixed and pressed

- $LiBH_4$ and Al_2O_3
- LiI and Al_2O_3
- AgI and Al_2O_3
- AgBr and Al_2O_3
- CuBr and Al_2O_3
- CuBr and TiO_2
- $Li_7La_3Zr_2O_{12}$ and Lithium borosilicate glass
- Lithium borate and SiO_2

glass ceramic

- $LiAlSiO_4$
- $AgI\text{-}Ag_2O\text{-}V_2O_3$

filled

- LiI and SiO_2

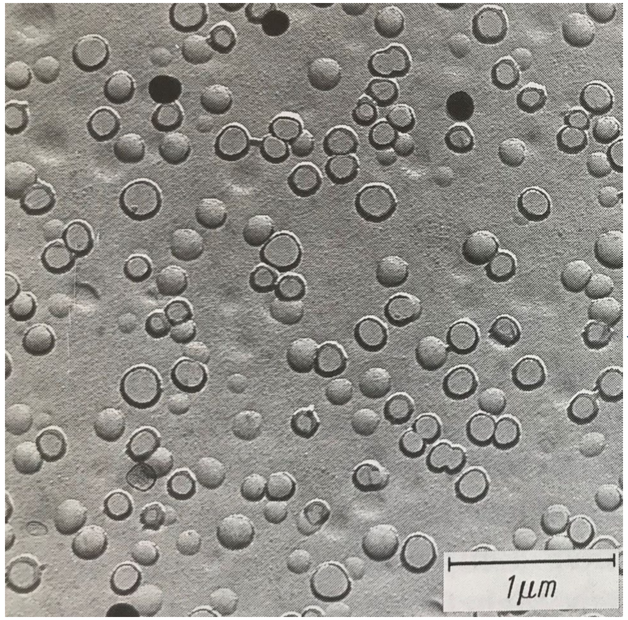
sputtered

- LiF and SiO_2

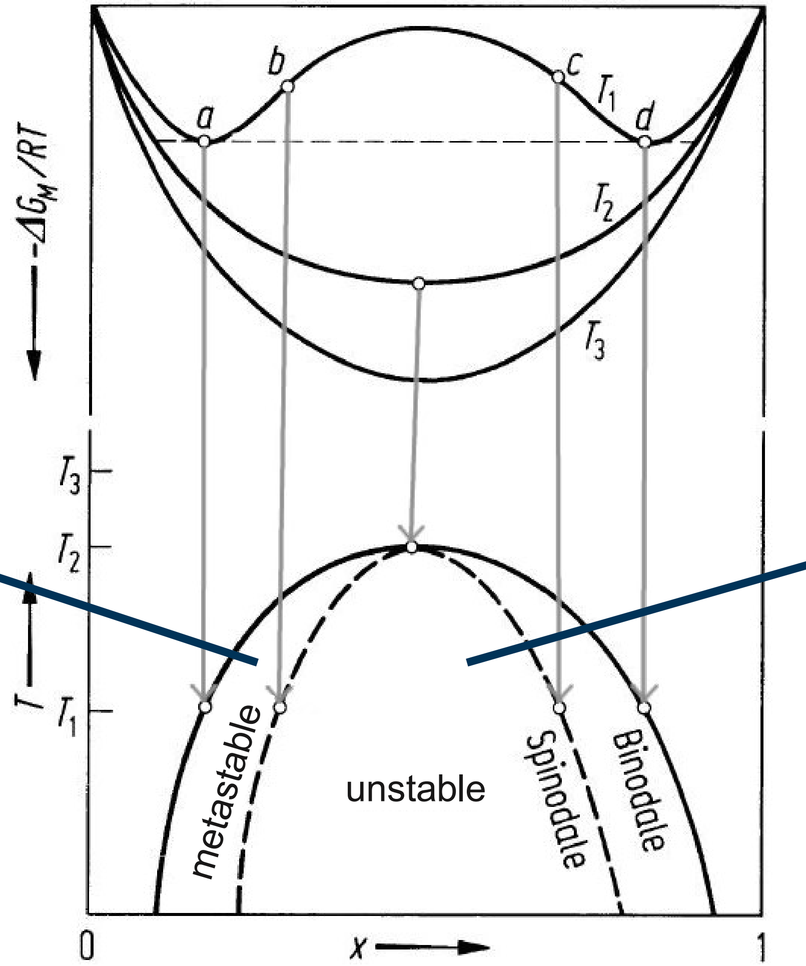
phase separation

- silver chalcogenide glasses

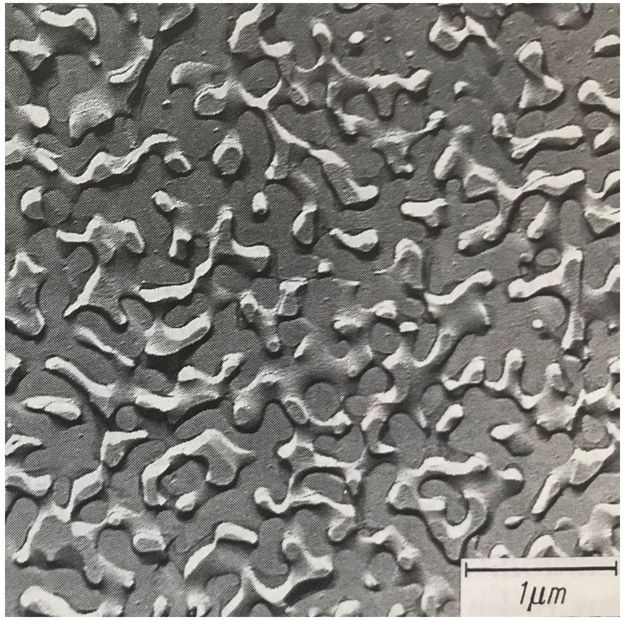
2. Phase Separation in Glasses



droplet segregation



free energy and segregation dome as a function of temperature and composition



two interconnected phases

3. Ionic Conduction in Glasses

Anderson-Stuart model

propability of ion movement = energy to change site + energy to deform network

<u>Site change energy</u>

$$E_{sc} \approx \frac{Z \cdot Z_N \cdot e^2}{r + r_O} - \frac{Z \cdot Z_N \cdot e^2}{\frac{\lambda}{2}} \approx \frac{-\beta}{\gamma} \cdot E_B$$

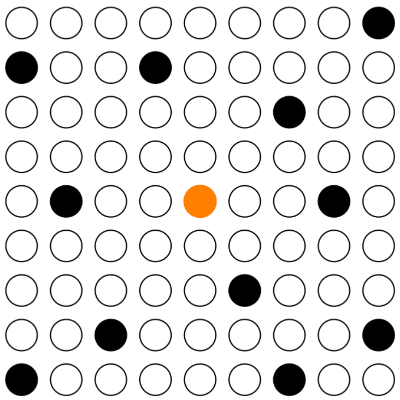
Z/Z_N … valence of involved ions
r/r_O … radius of involved ions
β … finite displacement factor
γ … polarisability of the oxygen atom
λ … lattice constant
E_B … binding energy

<u>Network strain energy</u>

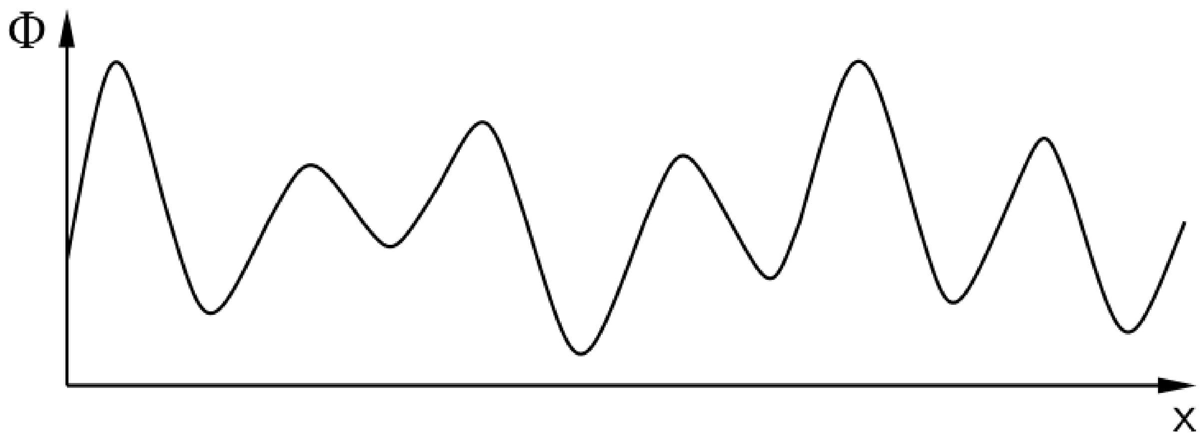
$$E_{nd} = \frac{1}{2} \cdot E_S = 4\pi \cdot G \cdot r_M (r - r_M)$$

G … shear modulus
r_M … radius of doorway
E_S … strain energy of close-packed liquids

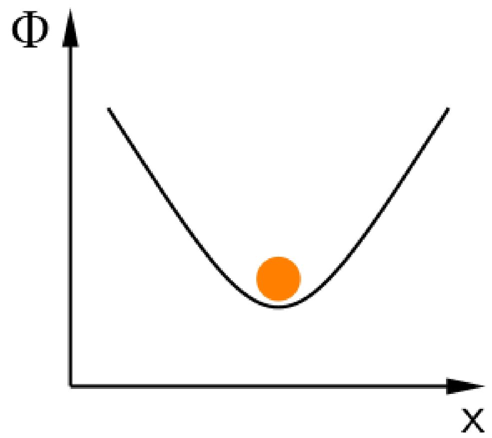
Jump relaxation model



sublattice of
mobile ions

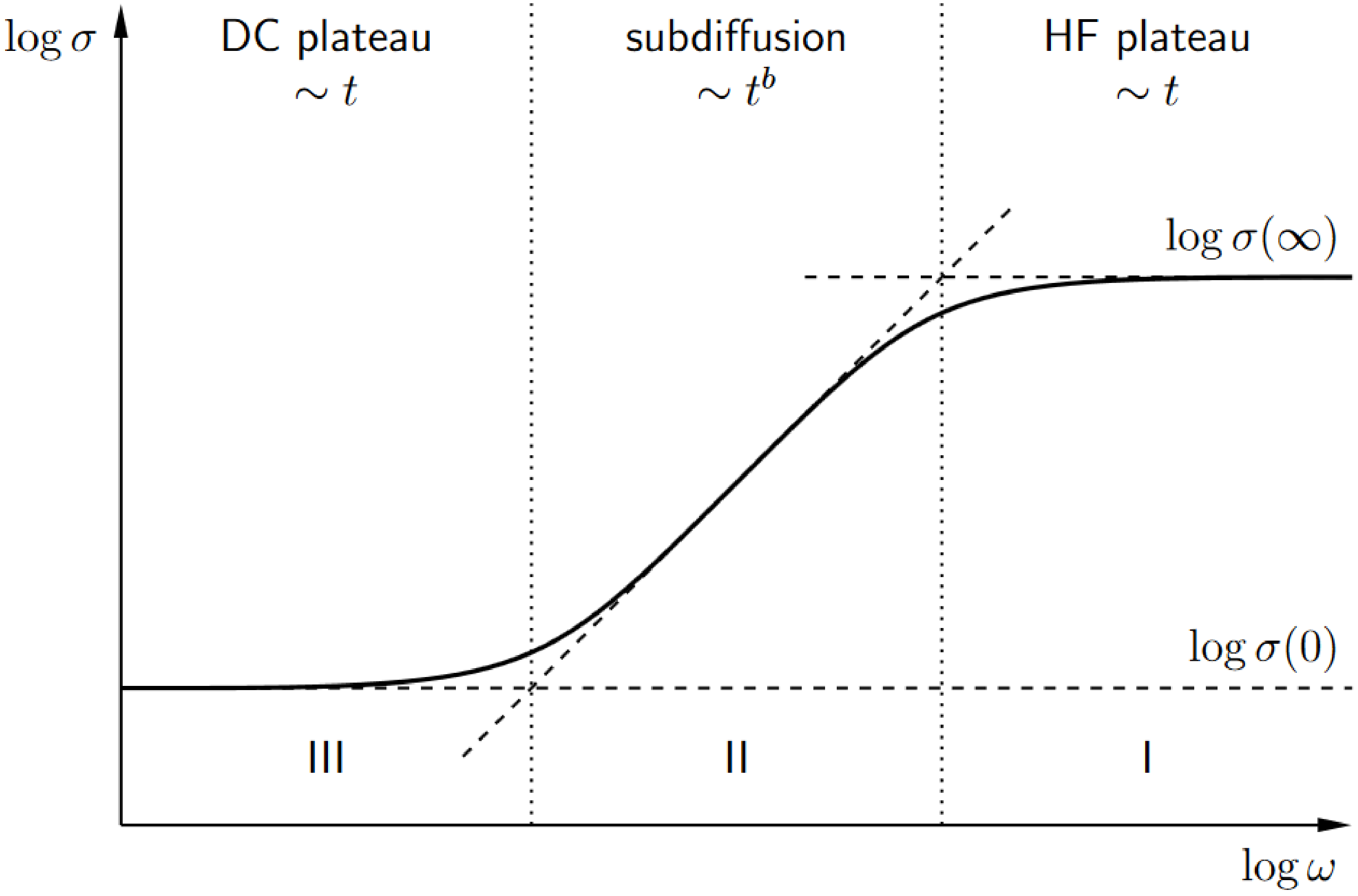


potential of immobile ions in glass



single potential of
mobile ion

Jump relaxation model



frequency dependence of conductivity (double logarithmic display)

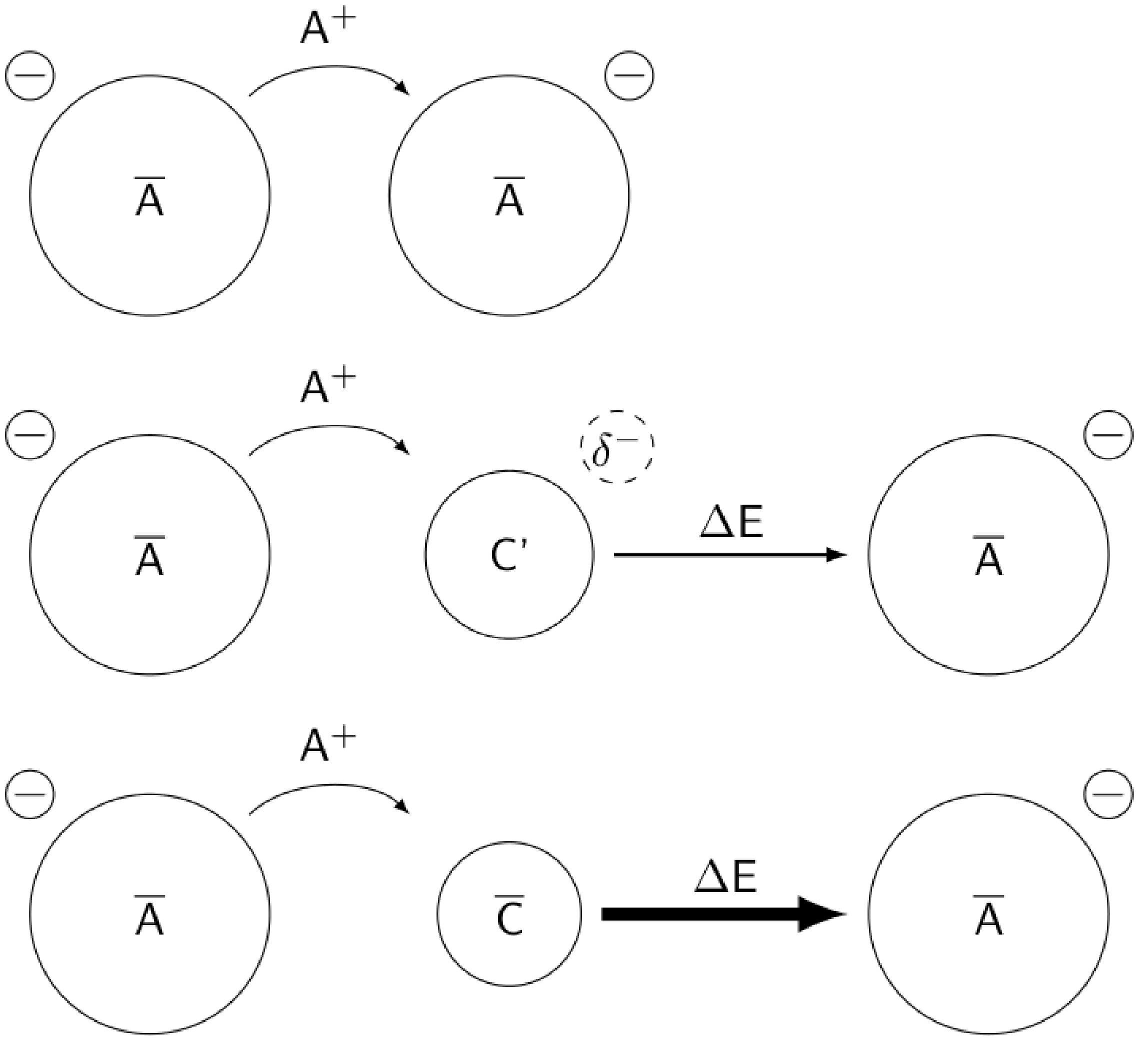
Dynamic structure model

A^+ … mobile ion

$\overline{A}$ … adapted site for A^+

C‘ … site near negativ charge (must be adapted)

$\overline{C}$ … site (must be adapted)



Ionic Conductivity of Lithium Borosilicate Glasses

- depending on:
    - temperature
    - Li^{+} concentration
    - number of NBO
    - molar volume
    - mixed glassformer effect?

- $\sigma \approx 10^{-8} \ldots 10^{-6}$ S/cm at 25 °C
- σ up to 10^{-2} S/cm at 200 °C

4. Methods

Melting

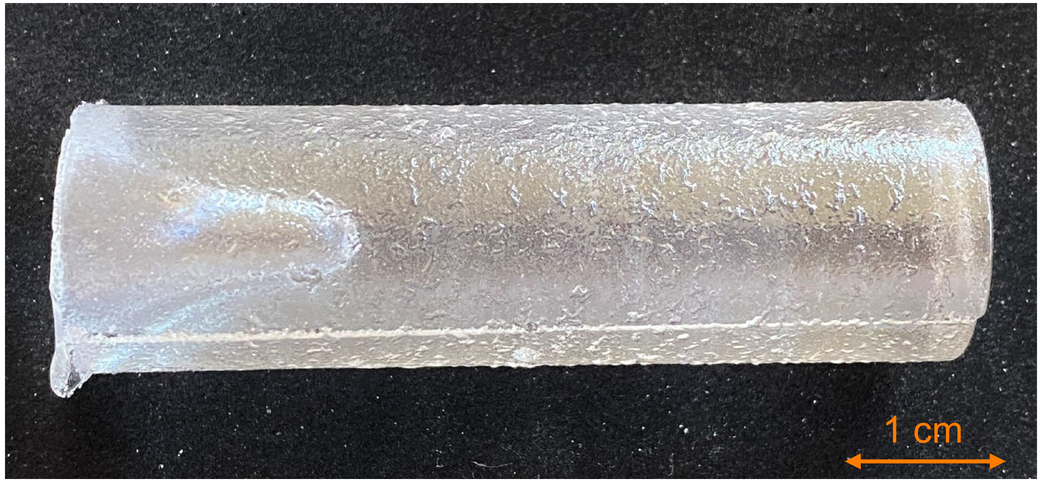
- temperature = 950 … 1300 °C
- time = 60 min
- cold/warm graphite mould

Planned Methods

- tempering (T_g + 50 K or + 150 K)
- impedance spectroscopy
- scanning electron microscopy
- Fourier-transform infrared spectroscopy

Differential Scanning Calorimetry

- temperature program: 2x 30 … 1000 … 30 °C
- heating/cooling rate: 10 K/min



22.4 mole% Li_2O, 57.6 mole% B_2O_3, 20 mole% SiO_2

Li_2O / B_2O_3 ≙ 28 / 72

5. Results (so far)

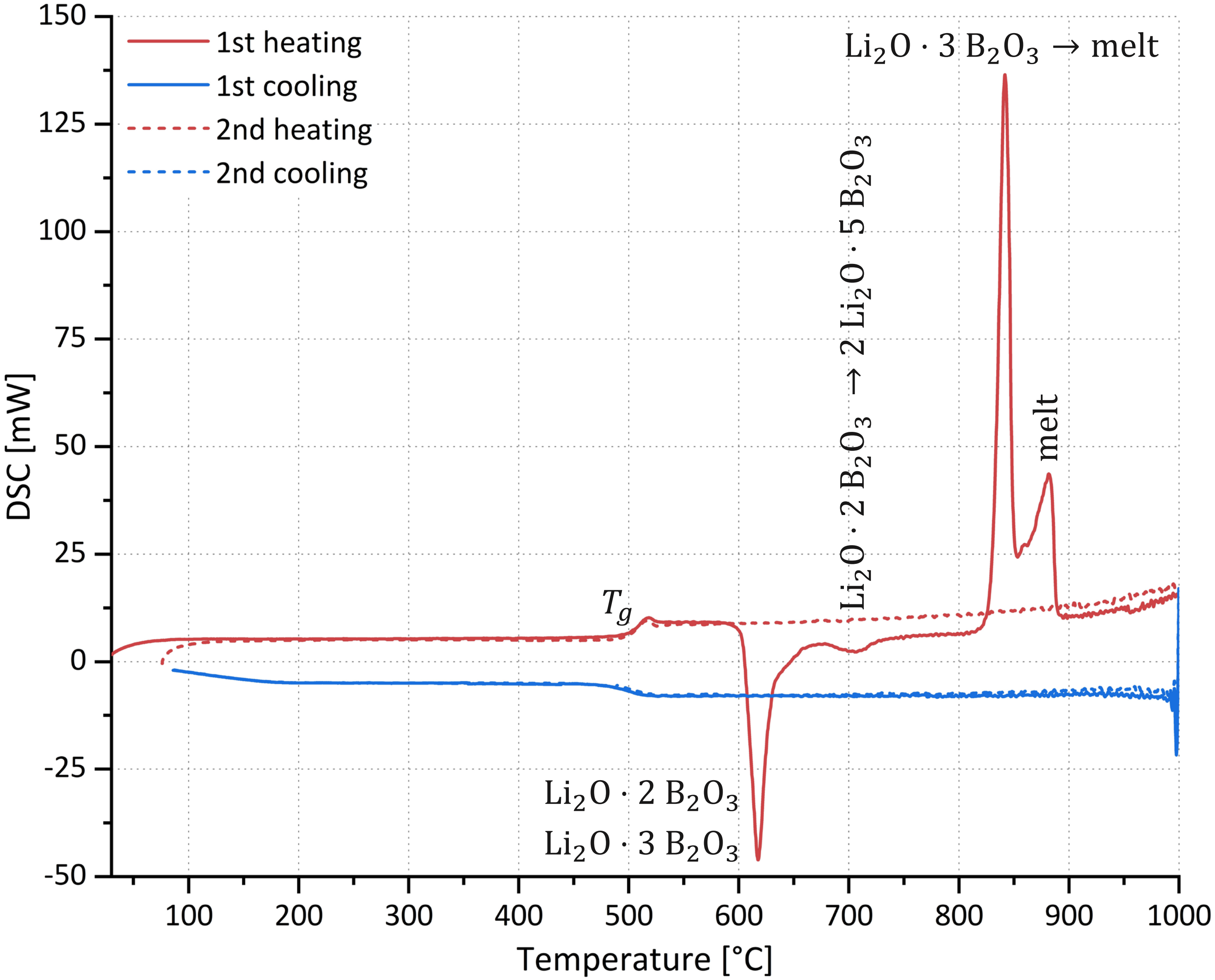
Differential Scanning Calorimetry

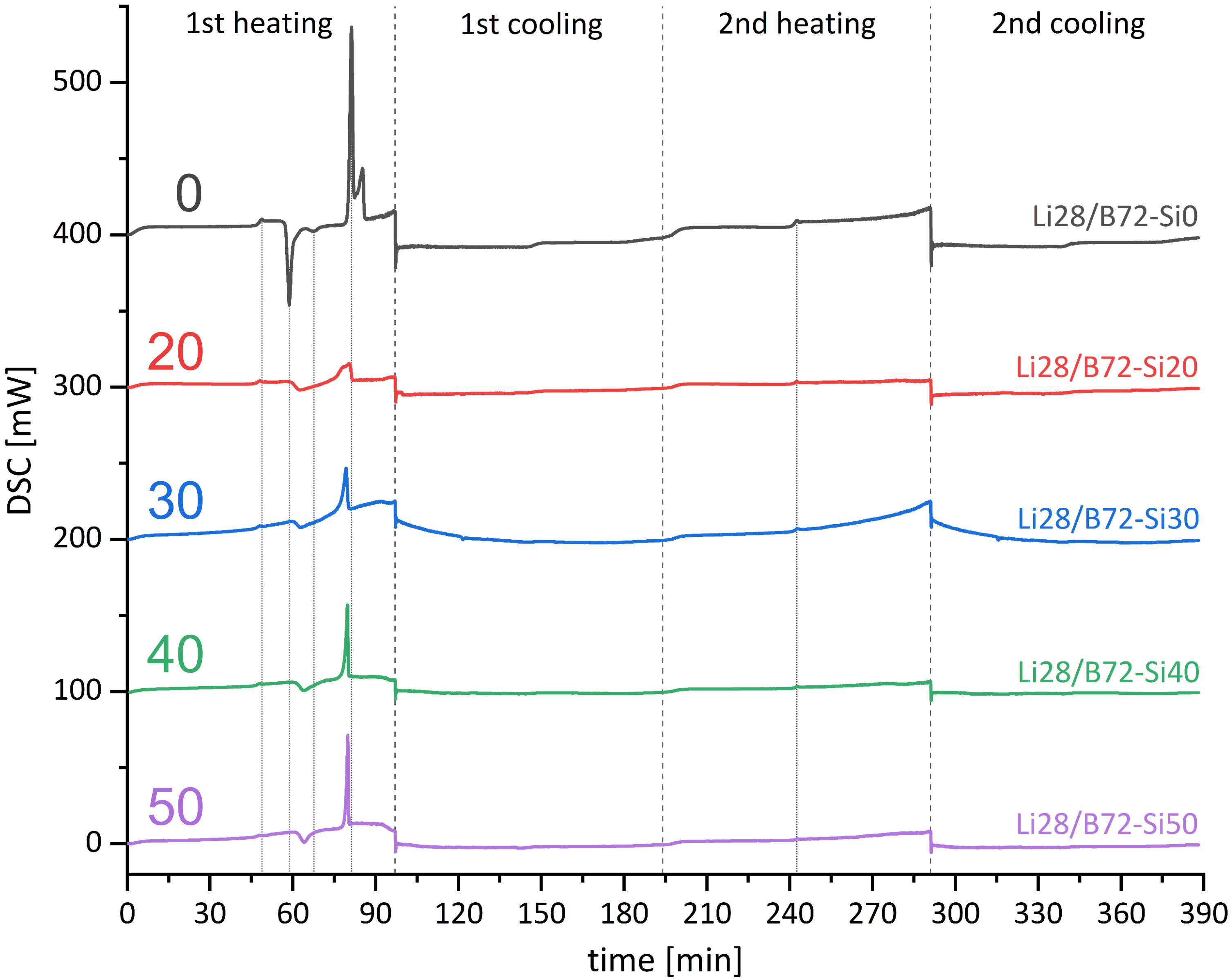
Sample composition:

28 mole% Li_2O

72 mole% B_2O_3

negative ≙ exotherm





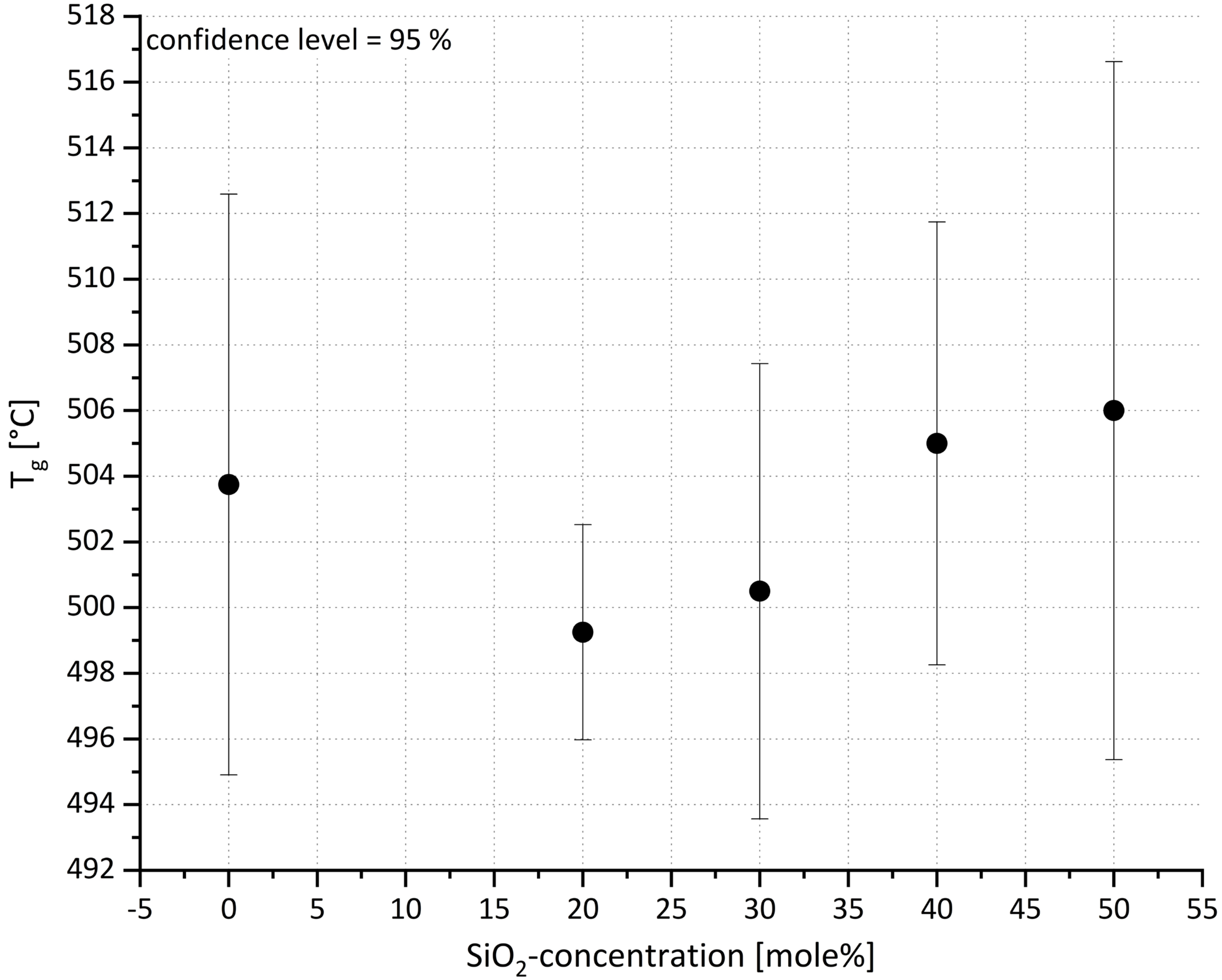
Differential Scanning Calorimetry

all samples:

Li_2O / B_2O_3 = 28 / 72 mole%

varying SiO_2 content

negative ≙ exotherm



Differential Scanning Calorimetry

all samples:

Li_2O / B_2O_3 = 28 / 72 mole%

varying SiO_2 content

6. Summary

- glasses conduct ions
- durable ion movement requires:
  - ion hop
  - relaxation of vicinity
- interfaces may enhance conductivity
- interfaces in lithium borosilcate glasses may be formed by phase separation

Next Steps:

- measuring setup for impedance spectroscopy
- tempering
- sample series with different Li_2O – B_2O_3 ratio

Thank you for your attention!

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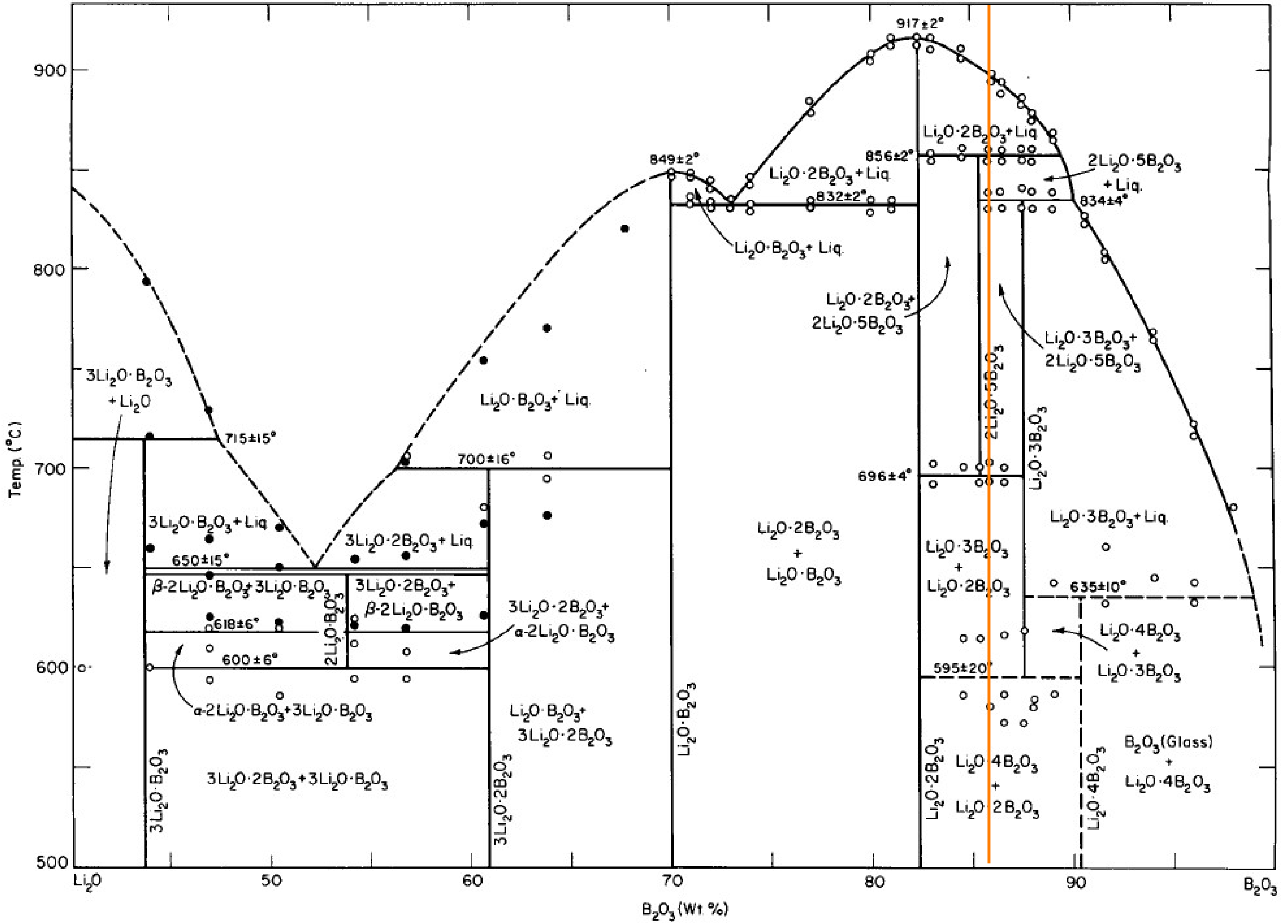
Phase diagram of Li_2O – B_2O_3



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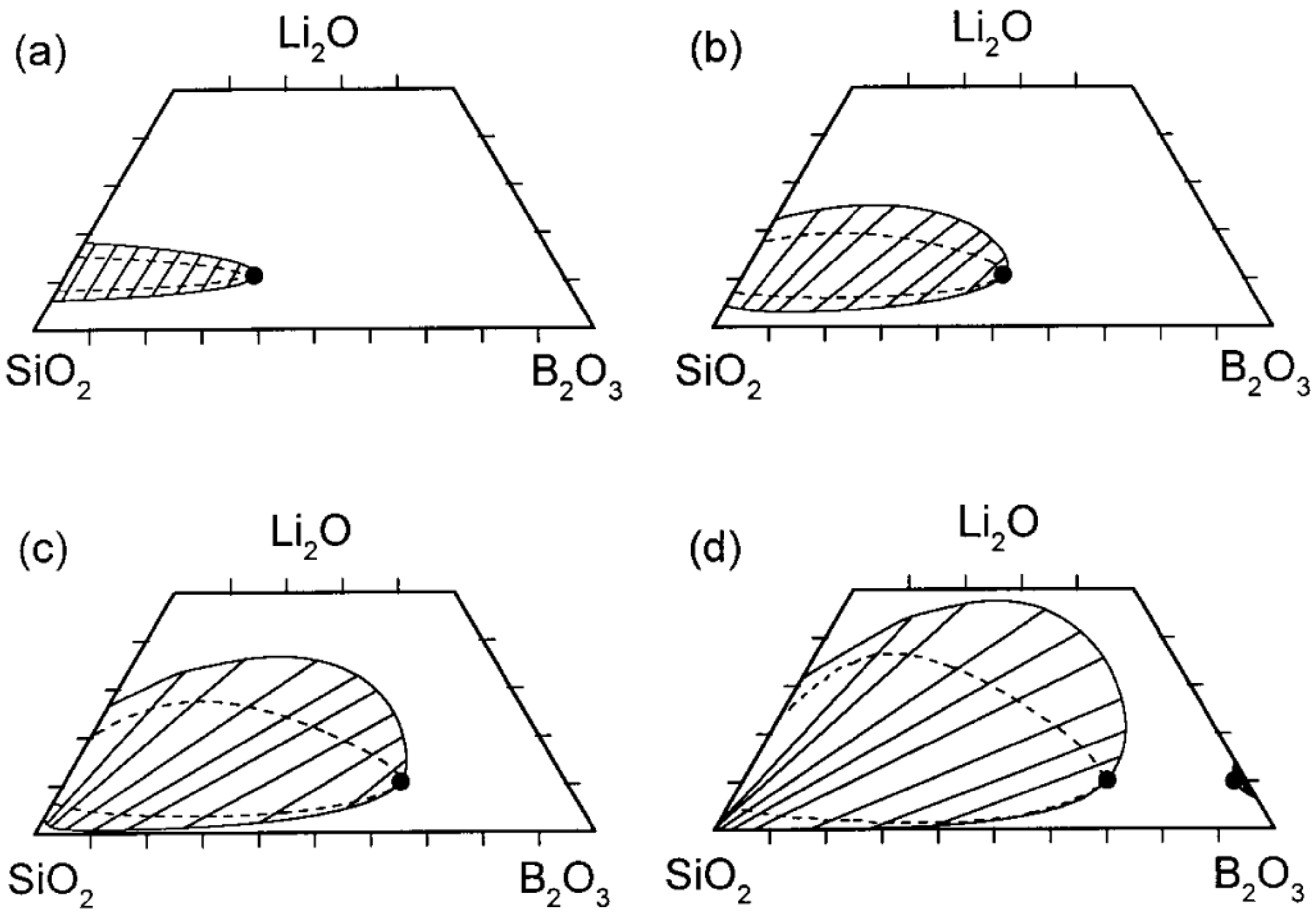

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