Summer 6-26-2005

XI, Part 1: Structure and dynamics of ion-exchanged glasses

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Structure and dynamics of ion-exchanged glasses

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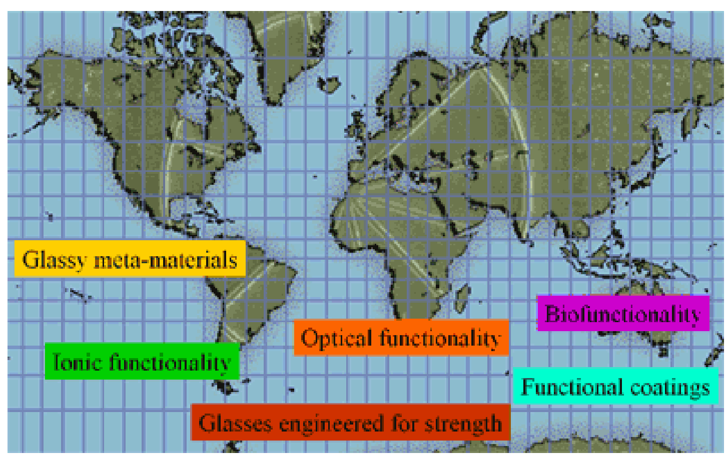
17th Universtity Conference on Glass Science

&

1st International Materials Institute Workshop on

NEW FUNCTIONALITY IN GLASSES

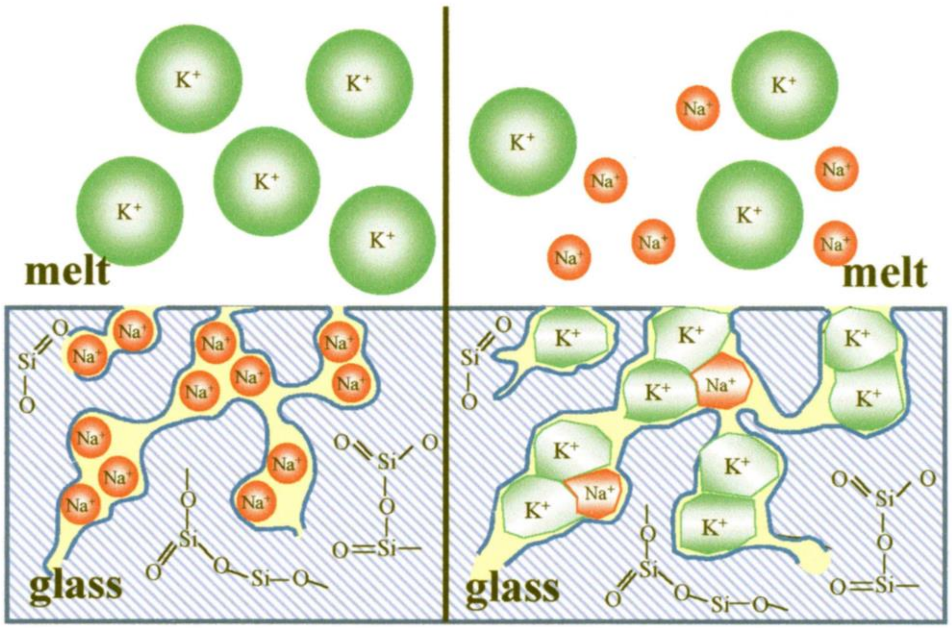


June 26-30, 2005 / State College, Pennsylvania

Outline of presentation

- Ion-exchange process: introduction & relevant literature
- Structure of ion-exchanged soda-lime-silica glass
- Structure of ion-exchanged $30Na_2O$-$70B_2O_3$ glass
- ac conductivity spectra of ion-exchanged $30Na_2O$-$70B_2O_3$ glass
- Summary

ION EXCHANGE PROCESS IN GLASS



(a) Before ion exchange (b) After ion exchange

ion "crowding"

⇓

compressive stress

⇓

permanent compression

$T<T_g$

M.E. Nordberg et. al. *J. Am. Ceram. Soc.* 47 (1964) 215.

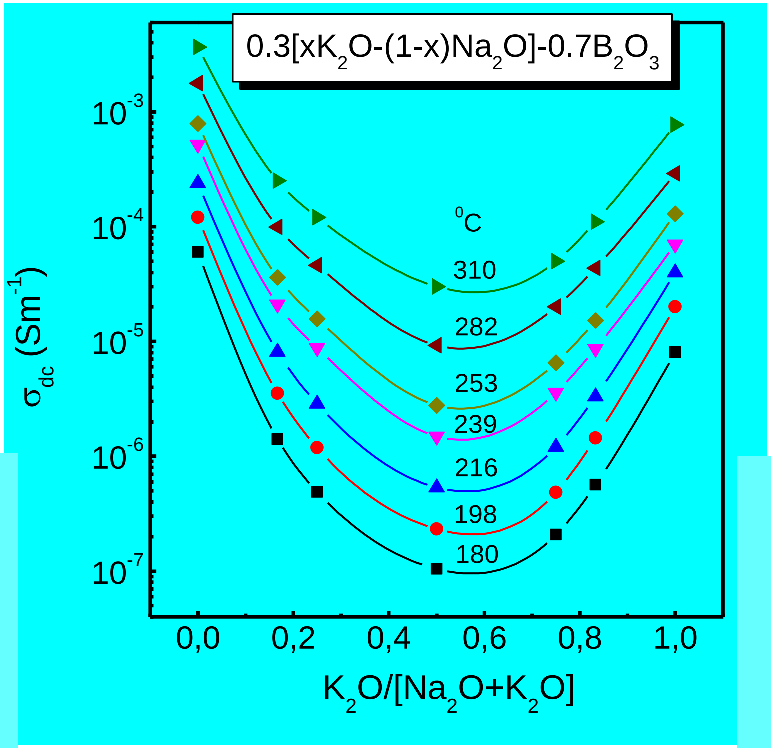
Applications:

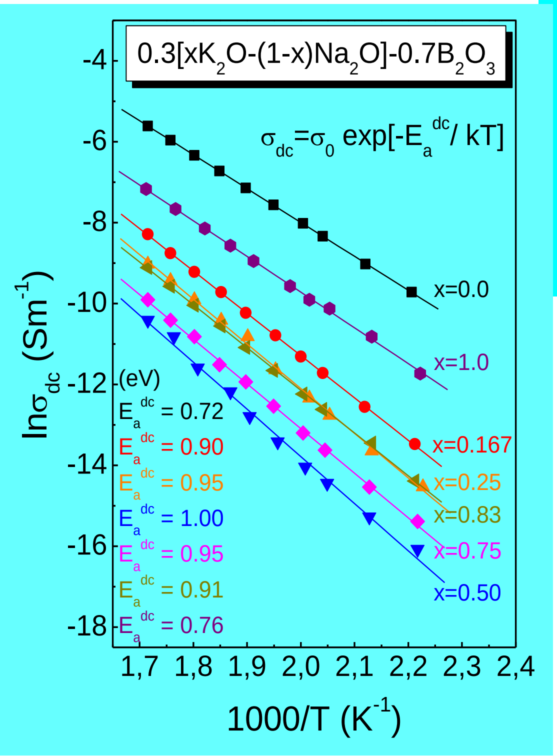
- Chemical strengthening of commercial silicate glass
- Altering optical properties of glass (waveguides, micro-optics)

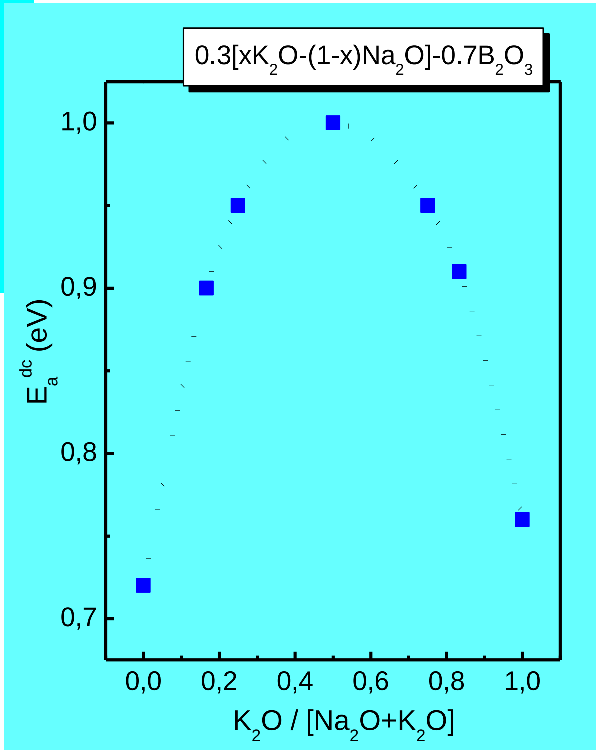
Open Questions:

- Is there a "mixed-alkali effect" in ion-exchanged glasses?
- How are K^+ ions accommodated within the glassy network?
- Can any changes in glass structure occur as a result of ion-exchange below T_g?

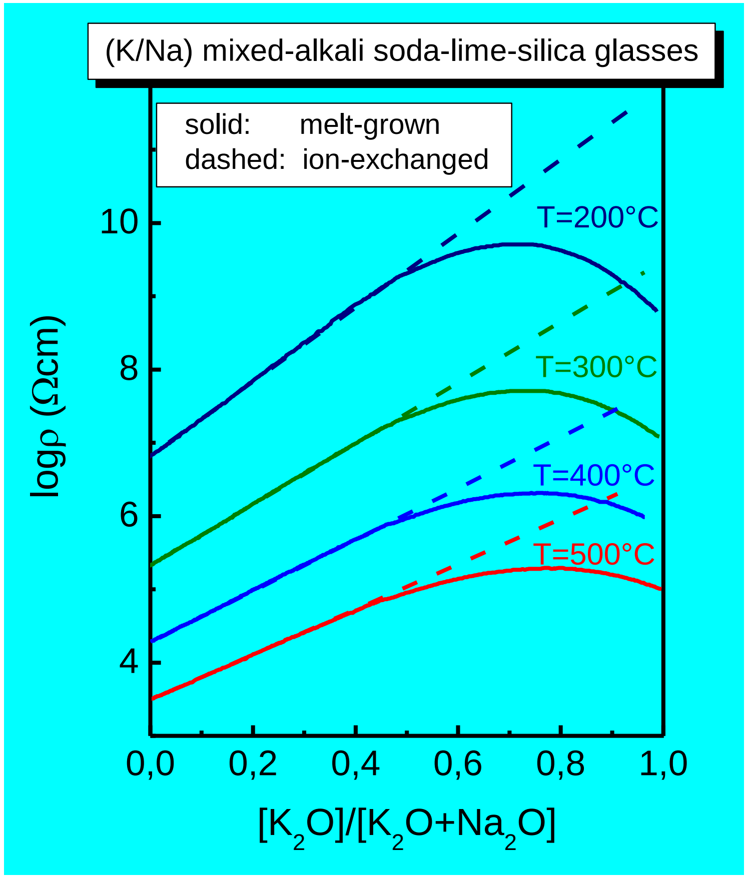
Mixed Alkali Effect (MAE) in melt-grown glasses







Mixed alkali glasses by ion exchange



G. Tomandl & H.A. Schaeffer, Non-Cryst. Solids, Trans. Tech. Publ., pp. 480-485 (1977).

⇒ Ion-exchanged glasses below T_g do not show the MAE; i.e. resistivity shows a linear behavior throughout the ion-exchanged layer

⇒ Ion-exchange below T_g generates a different “mixed-alkali structure” than the melting process.

Mixed alkali glasses by ion exchange, cont.

C. Windisch & W.M. Risen, J. Non-Cryst. Solids, 44, 345 (1981).

(Na/Li) ion-exchanged Li_2O-Al_2O_3-$2SiO_2$ glasses / Raman spectroscopy

⇒ Network structure of ion-exchanged glasses is different from that of melt-grown glasses of the same stoichiometry

⇒ Annealing the ion-exchanged glass leads to network structure identical to that of the melt-grown glass.

S.N. Houde-Walter, J.M. Inman, A.J. Dent & G.N. Greaves, J. Phys. Chem. 97, 9330 (1993).

(Ag/Na) ion-exchanged Na_2O-$4SiO_2$ glasses / X-ray absorption fine structure (XAFS)

⇒ CN (Na/O) ≈ 5, r(Na-O)=2.30-2.32 Å

⇒ CN (Ag/O) ≈2, r(Ag-O)=2.08-2.23 Å (very similar to the environment of Ag in Ag_2O)

⇒ metal ions create their own characteristic environments in glass.

G. Berg & A. Ludwig, J. Non-Cryst. Solids, 170, 109 (1994).

(Ag/Na) ion-exchanged soda-lime silica glass / ac conductivity (at 10^2, 10^3 Hz)

⇒ Concentration dependence of ac conductivity shows the typical mixed cation effect.

Mixed alkali glasses by ion exchange, cont.

T. Yano, K. Azegami, S. Shibata & M. Yamane, J. Non-Cryst. Solids, 222, 94 (1997).

(Ag/Na) ion-exchanged Na_2O-$2SiO_2$ glasses / X-ray photoelectron spectr. (XPS) & ^{29}Si-NMR

⇒ Ag ions induced a large charge redistribution on the glass network & an anomalous change in the distribution of Q^n silicate units

⇒ formation of Q^2 units at the expense of Q^3 units, but no Q^4 formation.

Y-K. Lee, Y.L. Peng & M. Tomozawa, J. Non-Cryst. Solids, 222, 125 (1997).

(K/Na) ion-exchanged soda-lime glass / FT-IR reflectance spectroscopy

⇒ Shift of the 1050 cm^{-1} peak is much larger than that caused by changes of the fictive temperature or composition. Thus, the shift of 1050 cm^{-1} peak is due mainly to the stress.

⇒ A new peak at 950 cm^{-1} develops with ion-exchange and is attributed to formation of non-bridging oxygen atoms.

M. Dubiel, B. Roling & M. Futing, J. Non-Cryst. Solids, 331, 11 (2003).

(K/Na) ion-exchanged soda-lime glass / ac conductivity spectroscopy (10^{-2} to 10^6 Hz)

⇒ No MAE for ion-exchange below T_g; but presence of MAE for ion-exchange slightly above T_g

⇒ Spectral shape of ac conductivity indicates differences in the ion dynamics between glasses exchanged slightly above T_g and the corresponding melt-grown glasses.

EXPERIMENTAL DETAILS…

GLASS COMPOSITIONS & SPECTROSCOPIC TECHNIQUES

Glass Compositions Investigated (mol%)		
A. Soda-Lime-Silica Glasses		
Oxide	**Pilkington float glass (T_g=558 ^{0}C) (FGS0)**	**Soft glass tubing (T0)**
SiO_2	71.78	71.62
Na_2O	12.44	14.02
CaO	8.76	6.19
K_2O	0.38	1.03
MgO	5.88	4.82
BaO	none	1.50
Al_2O_3	0.58	1.49
Fe_2O_3	0.04	0.02
SO_3	0.14	0.22
B. Sodium-Borate Glass: $30Na_2O$-$70B_2O_3$ (T_g=477 ^{0}C)		

INFRARED SPECTRAL MEASUREMENTS:

- Specular reflectance at quasinormal incidence (11^0)

⇒ use the same sample for continuous date acquisition in the mid- & far-IR range

(25-5,000 cm^{-1})

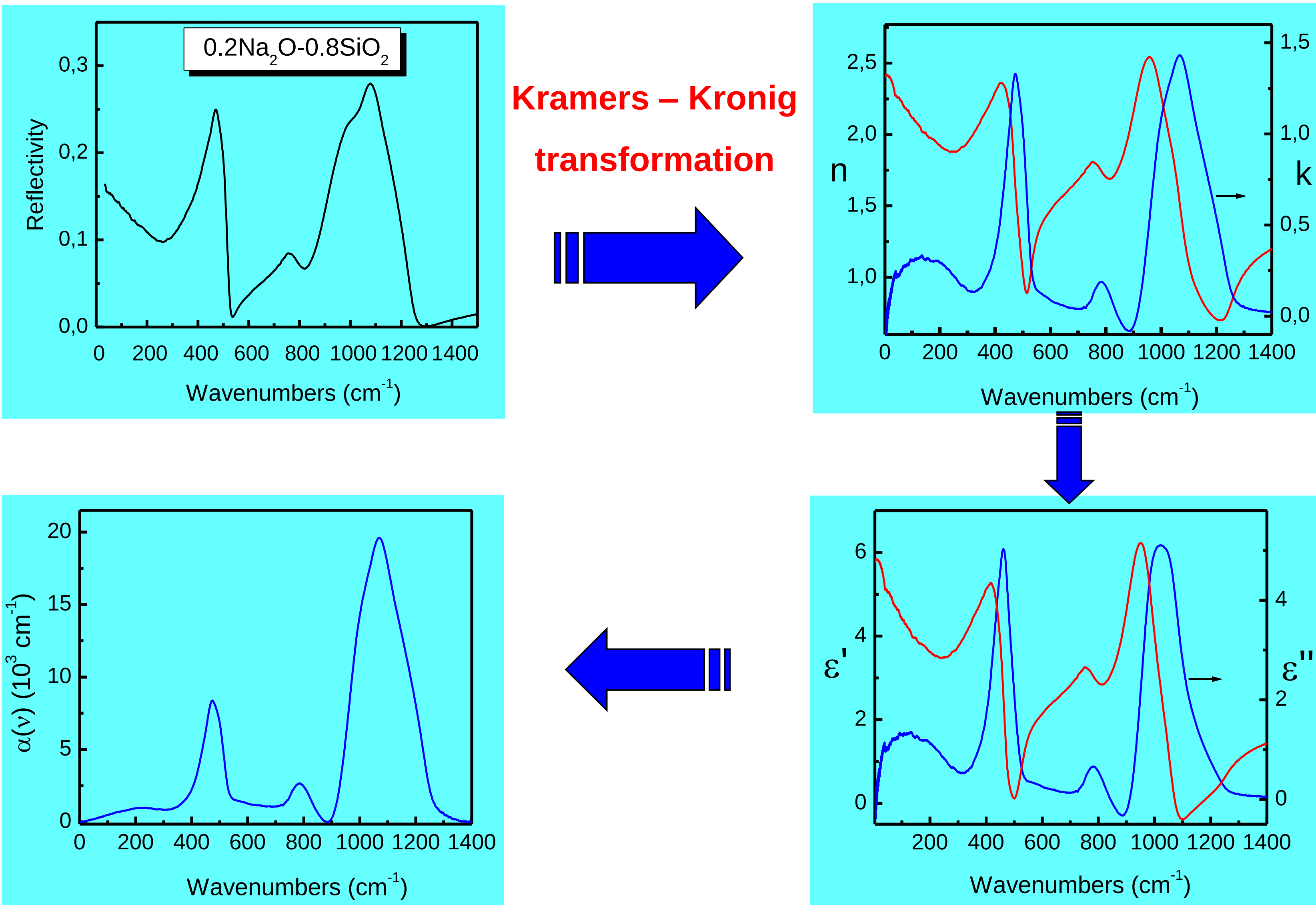
IMPEDANCE MEASUREMENTS:

- 5Hz -10MHz, f(T)

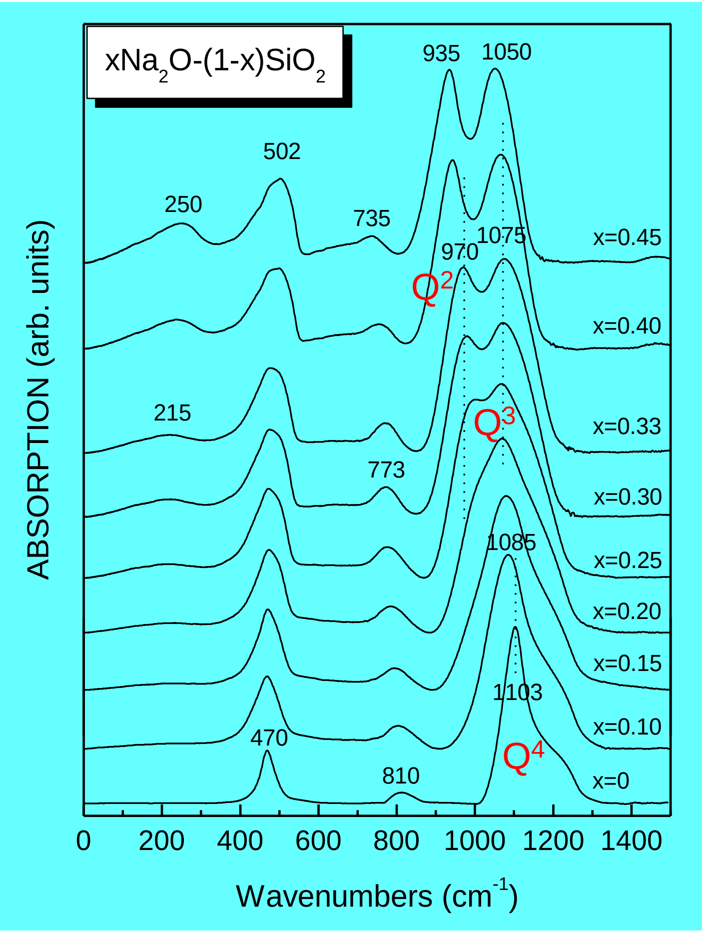
ELECTRON MICROPROBE ANALYSIS:

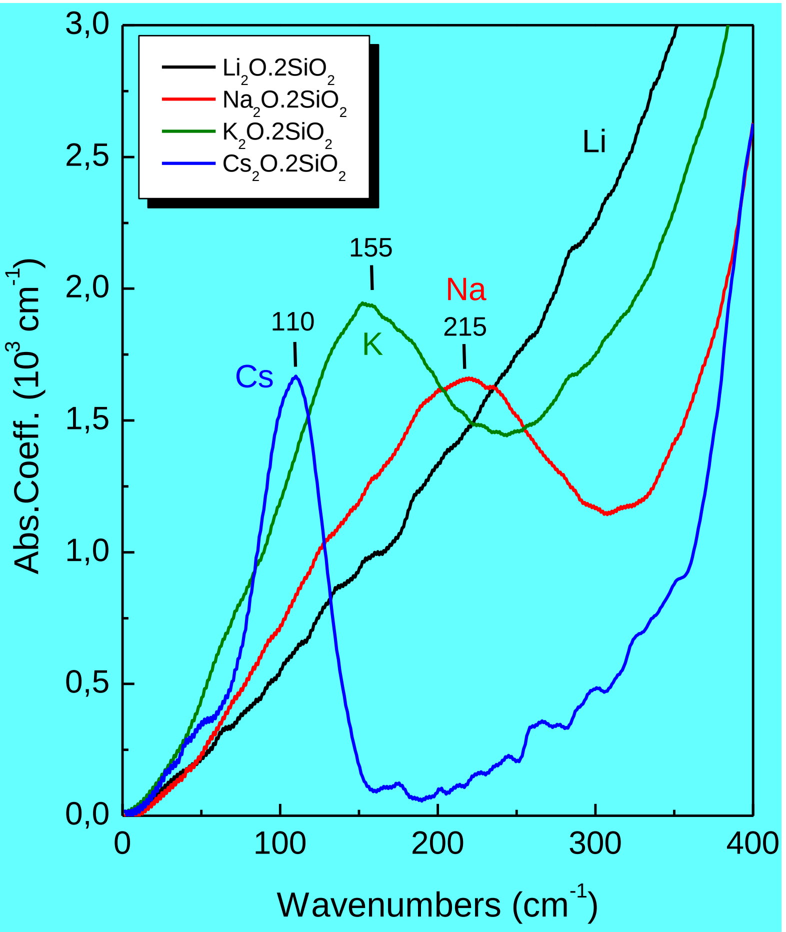
- K, Na profiles (Na K_α& K K_α X-rays produced by a 15 kV, 20-50 nA, e-beam)

ANALYSIS OF REFLECTIVITY SPECTRA



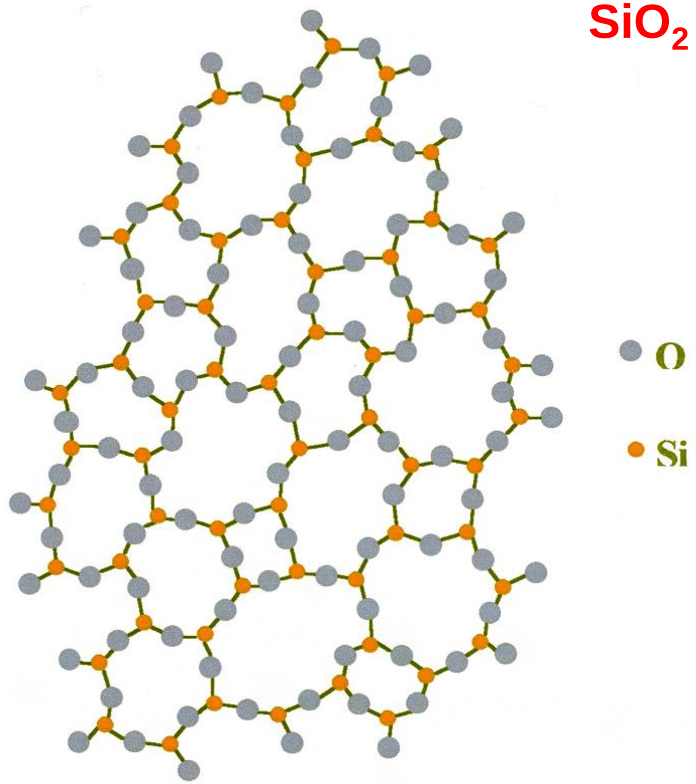
Short-range order structure and metal ion-site vibrations in silicate glasses





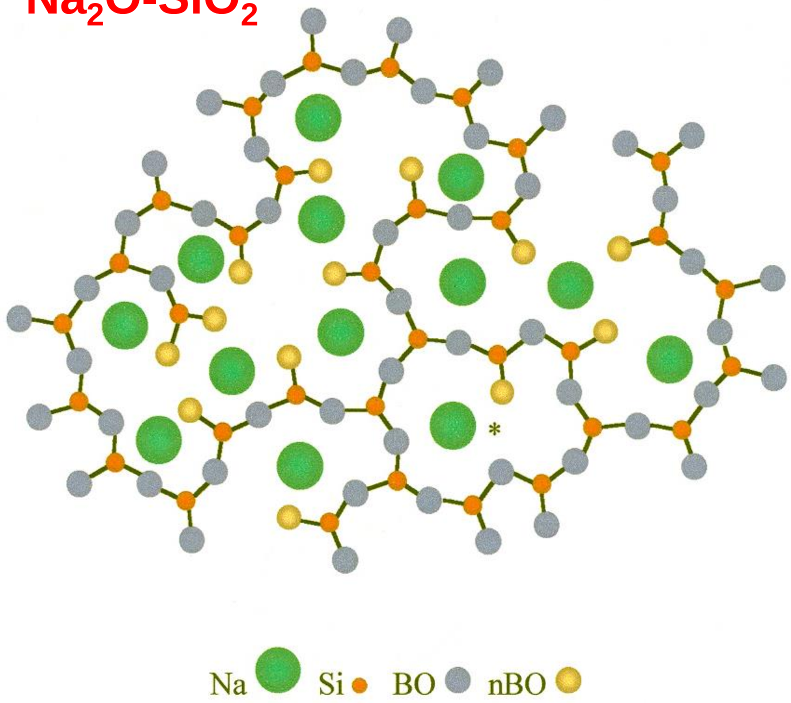
Continuous Random Network (CRN) Model

SiO_2



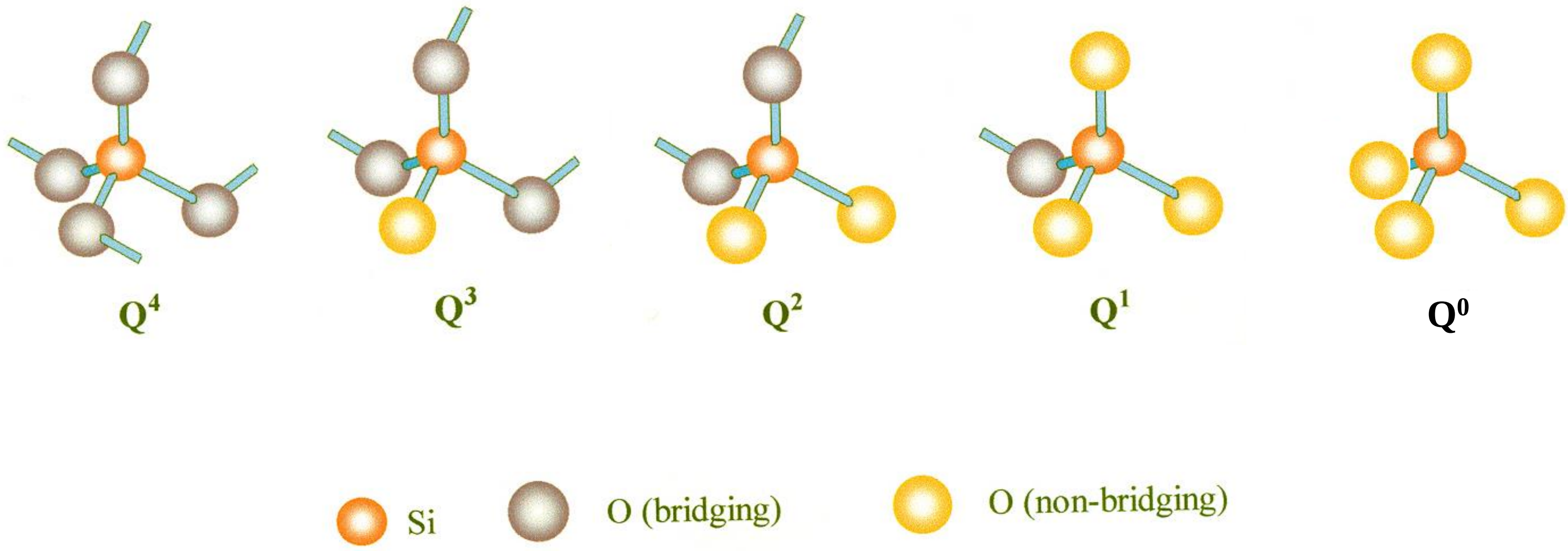
Zachariasen, 1932

Na_2O-SiO_2

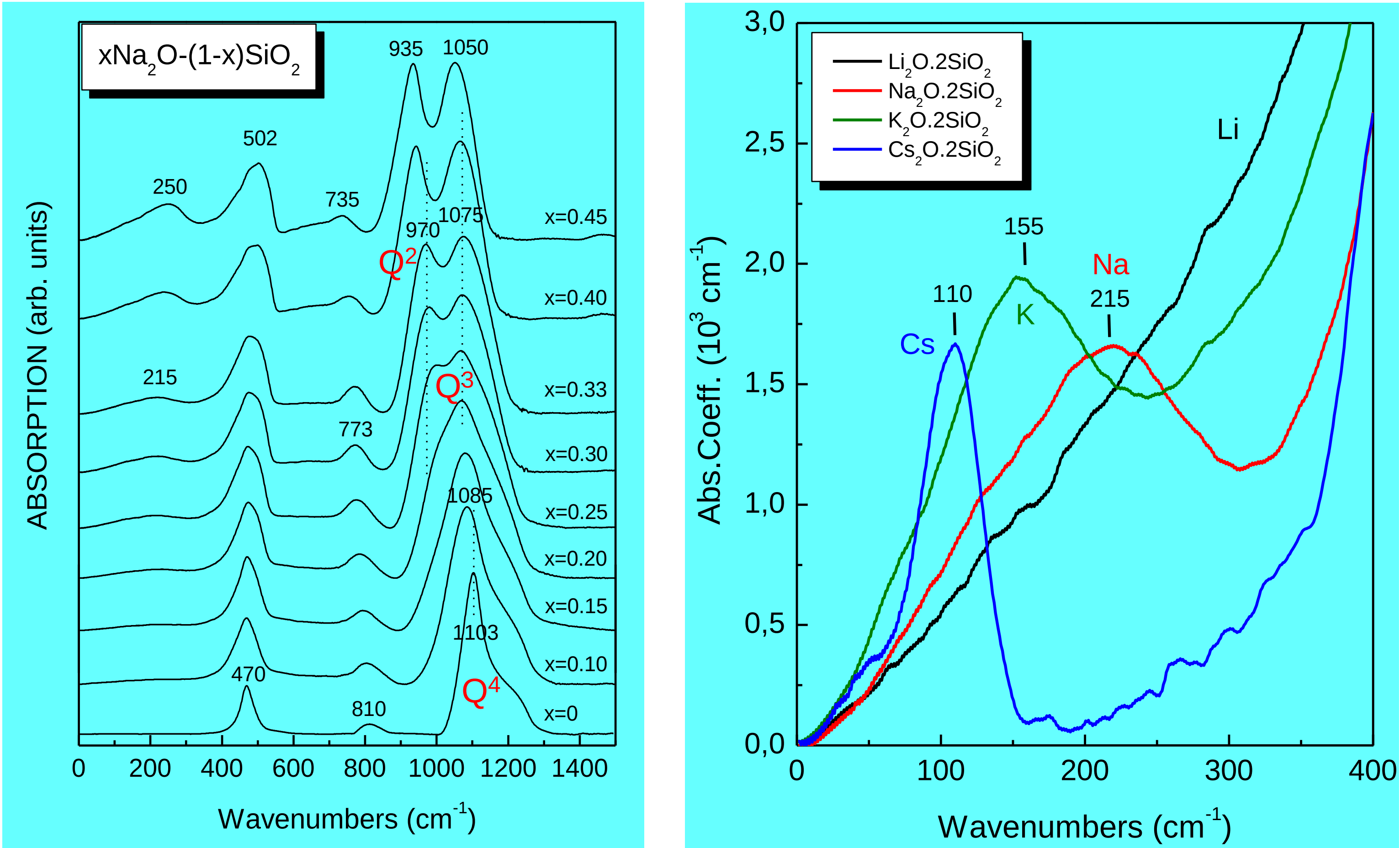


Warren-Biscoe, 1938

Q^n tetrahedral units in silicate glasses

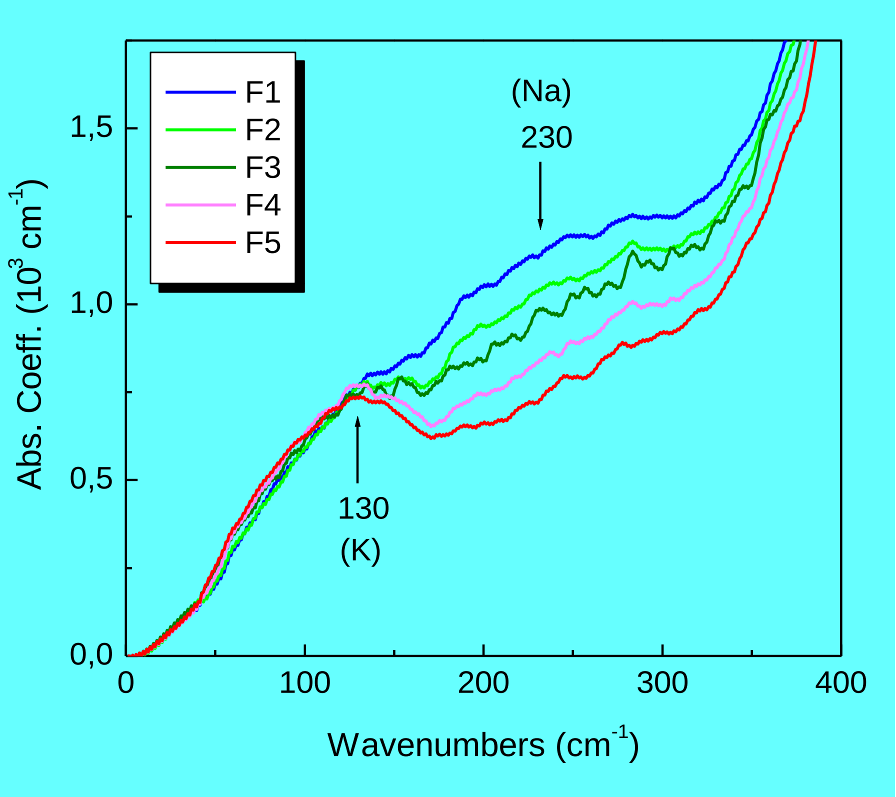


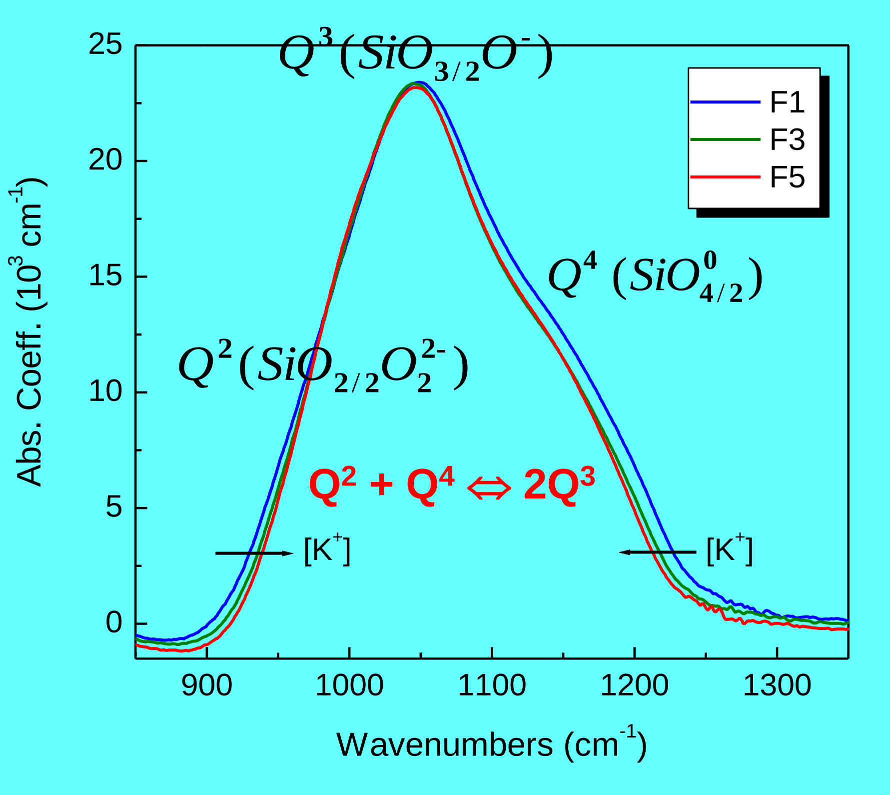
Short-range order structure and metal ion-site vibrations in silicate glasses



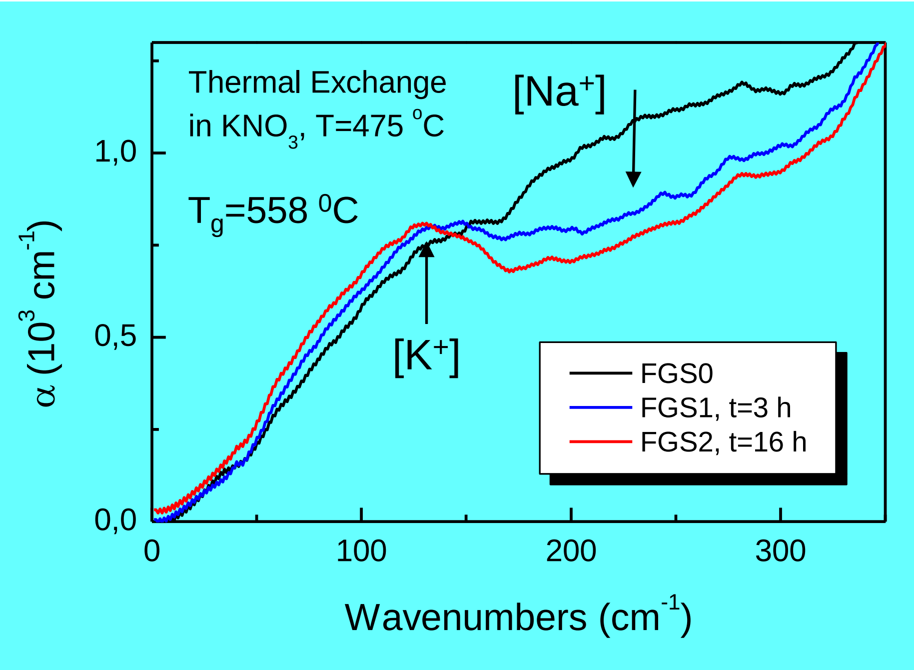
IR SPECTRA OF "SYNTHETIC" MIXED-CATION (Na^+/K^+) FLOAT GLASSES

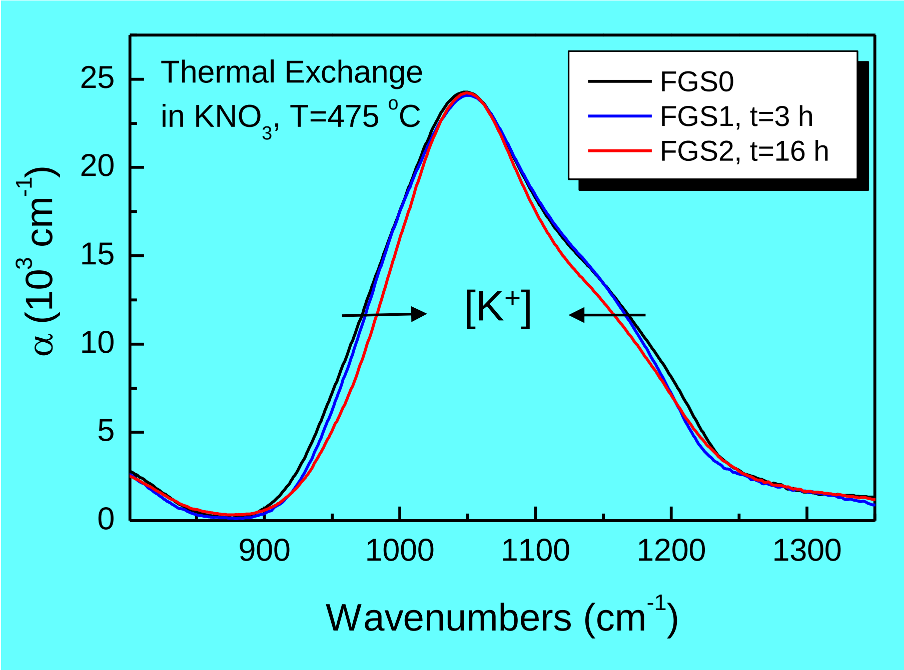
"Synthetic" float glasses					
mol%	F1	F2	F3	F4	F5
Na_2O	12.44	9.61	6.41	3.21	0.38
K_2O	0.38	3.21	6.41	9.61	12.44

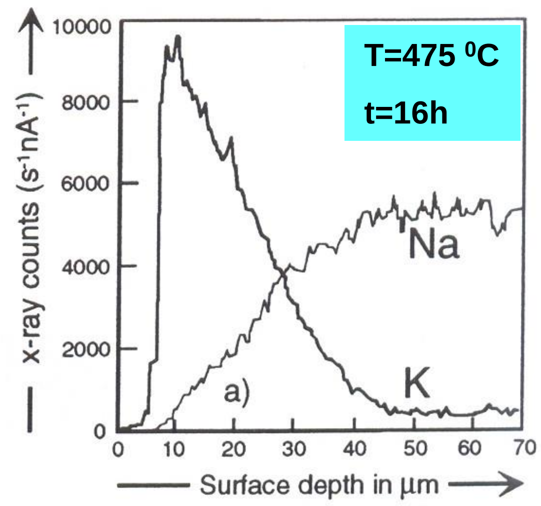




THERMALLY ION-EXCHANGED FLOAT GLASS: K^+/Na^+



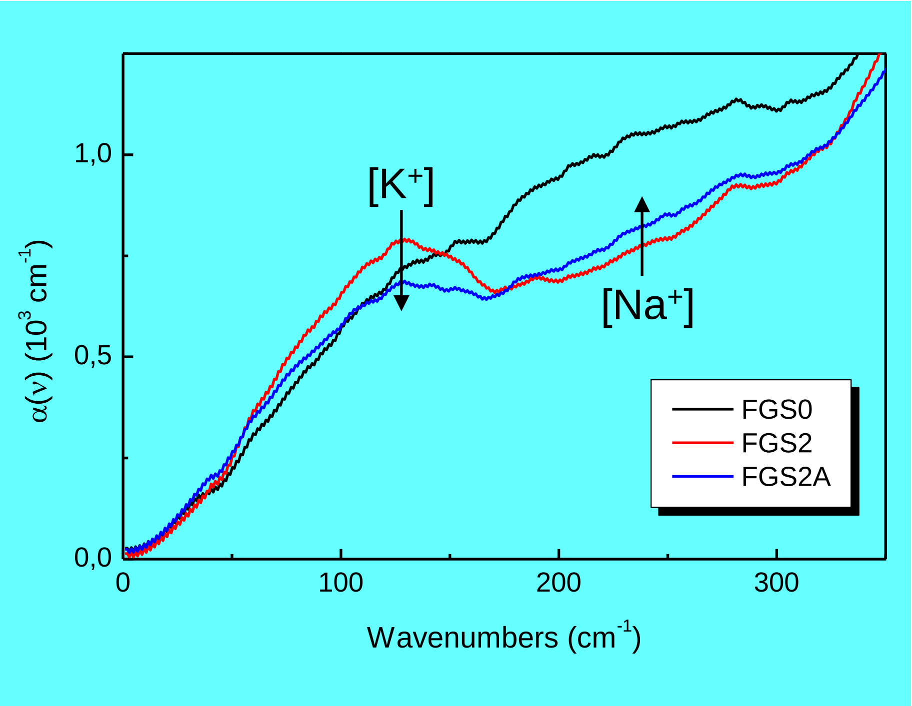


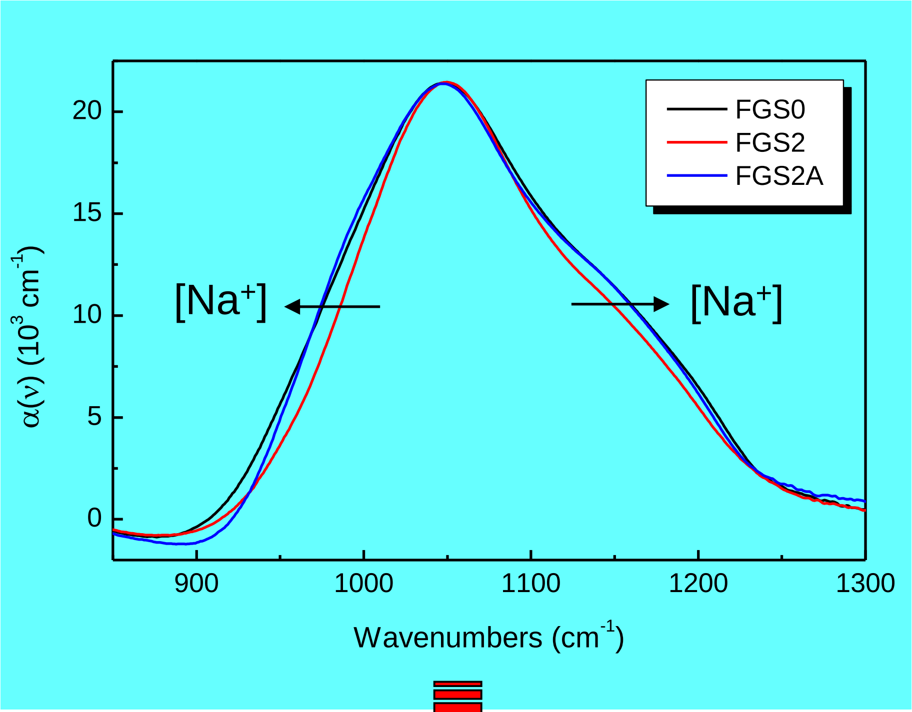


$Q^2 + Q^4 \Leftrightarrow 2Q^3$

glass structure becomes more homogeneous

ANNEALING OF ION-EXCHANGED (K^+/Na^+) FLOAT GLASS





FGS0: pristine float glass

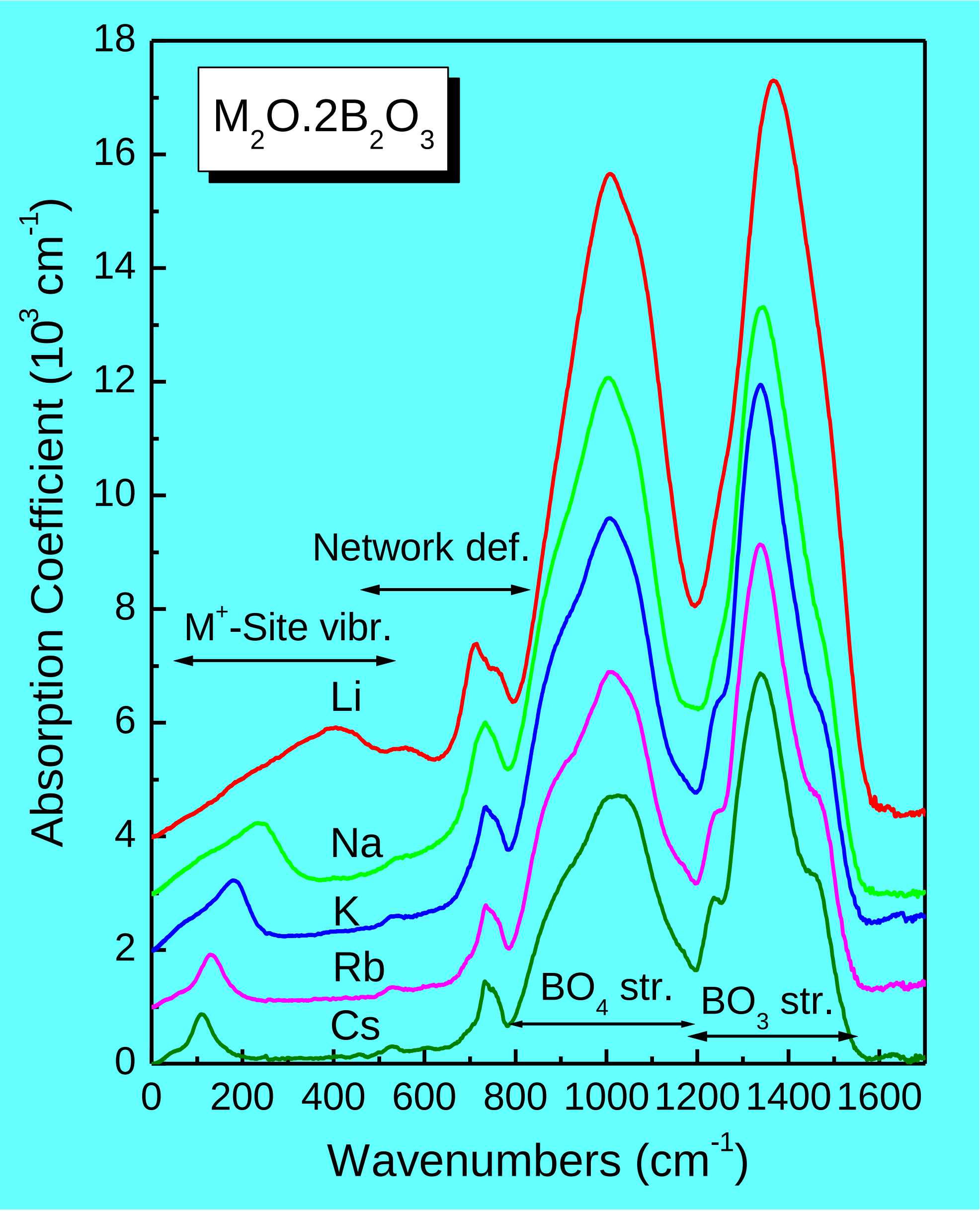
FGS2: FGS0 thermally exchanged in KNO_3 at 475 ^{0}C for 16h

FGS2A: FGS2 annealed in air at 475 ^{0}C for 16 h

$2Q^3 \Leftrightarrow Q^2 + Q^4$

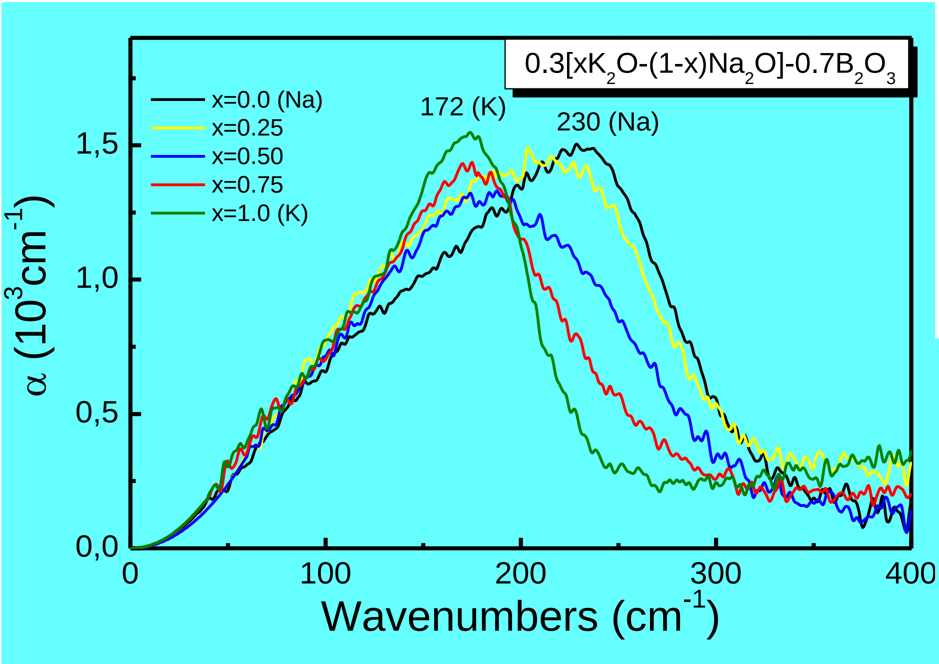
glass structure becomes less homogeneous

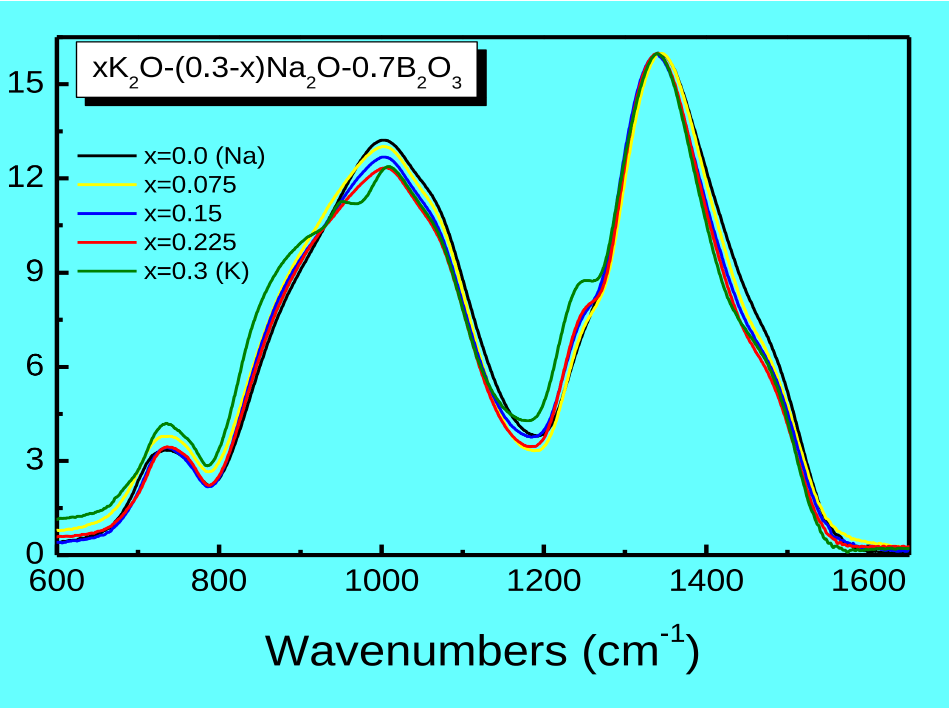
Infrared spectra of singe alkali borate glasses



IR SPECTRA OF "SYNTHETIC" MIXED-CATION BORATE GLASSES

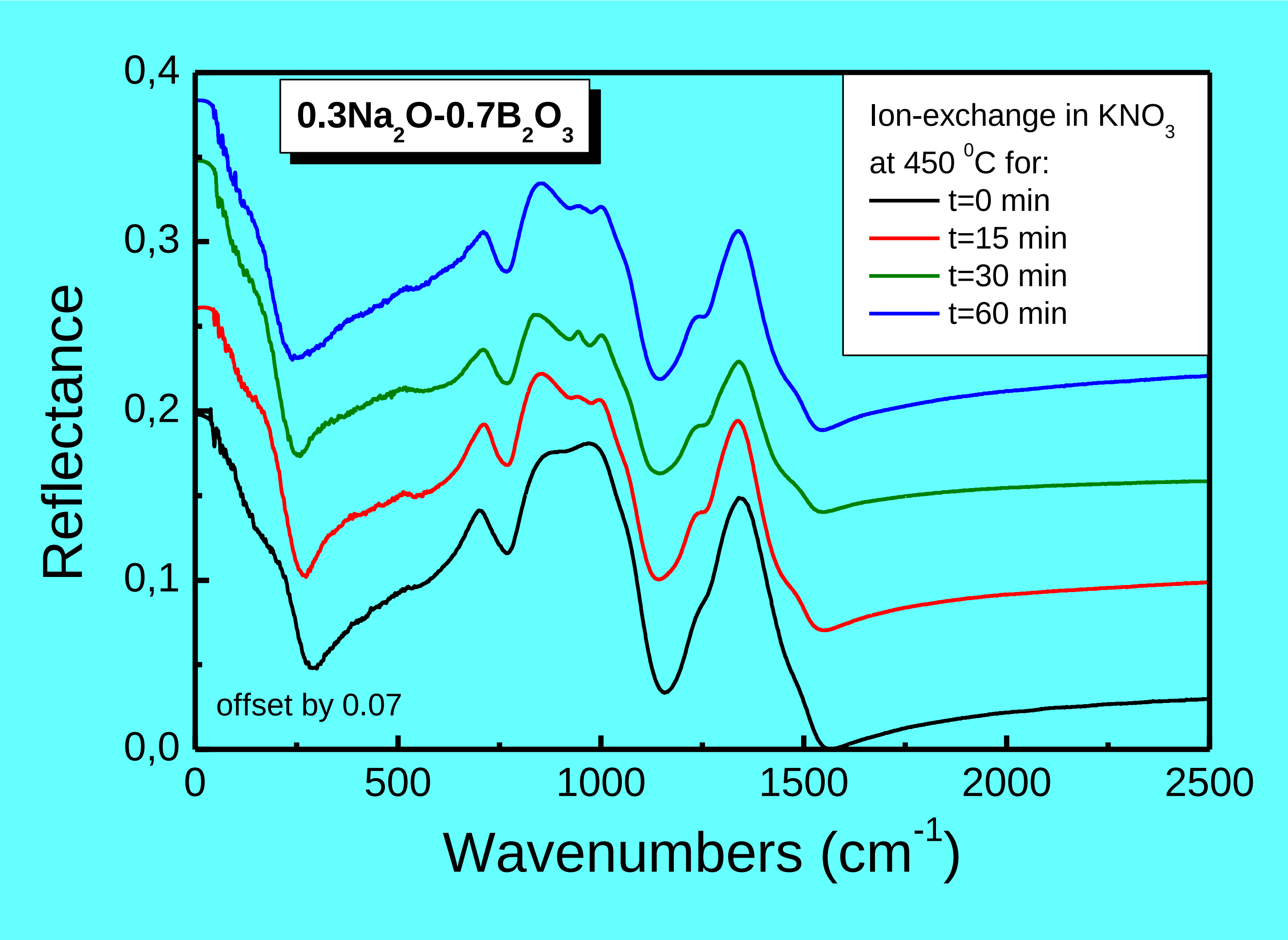
$0.3[xK_2O-(1-x)Na_2O]-0.7B_2O_3$



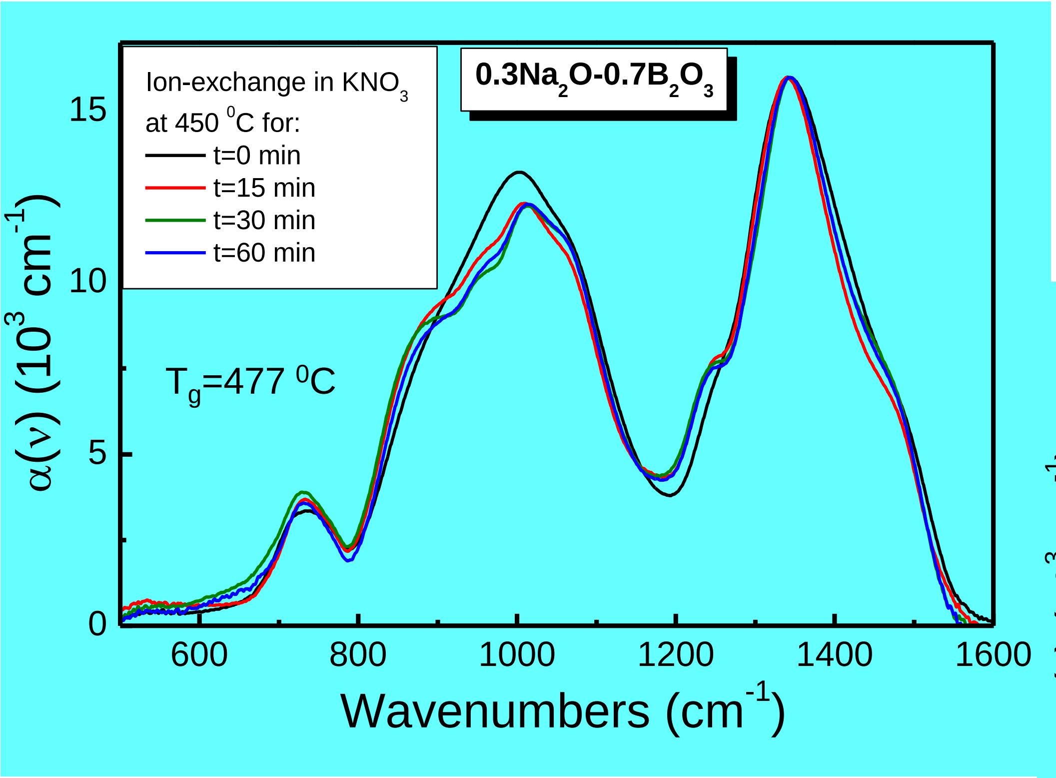


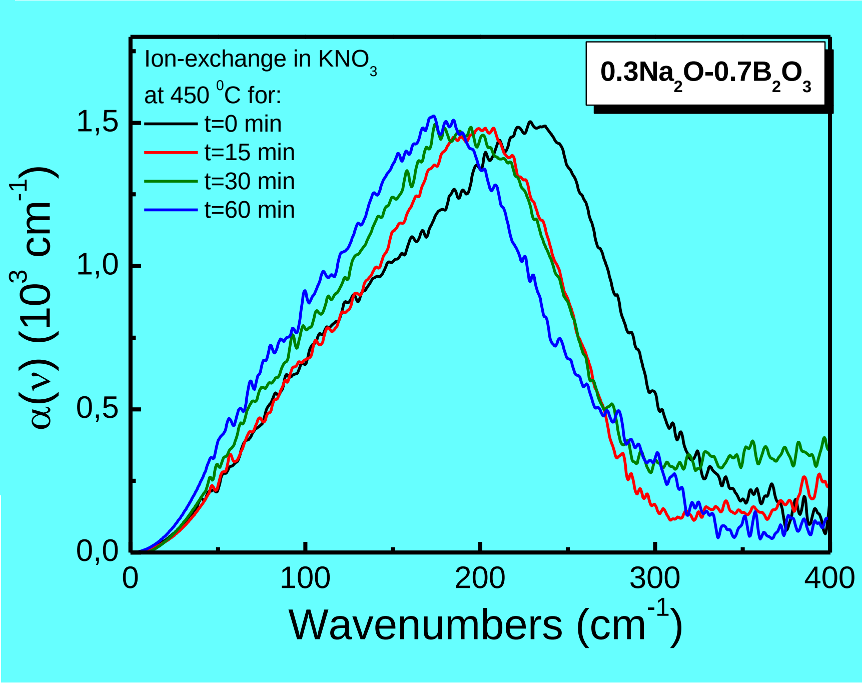
THERMALLY ION-EXCHANGED $0.3Na_2O$-$0.7B_2O_3$ GLASS: K^+/Na^+

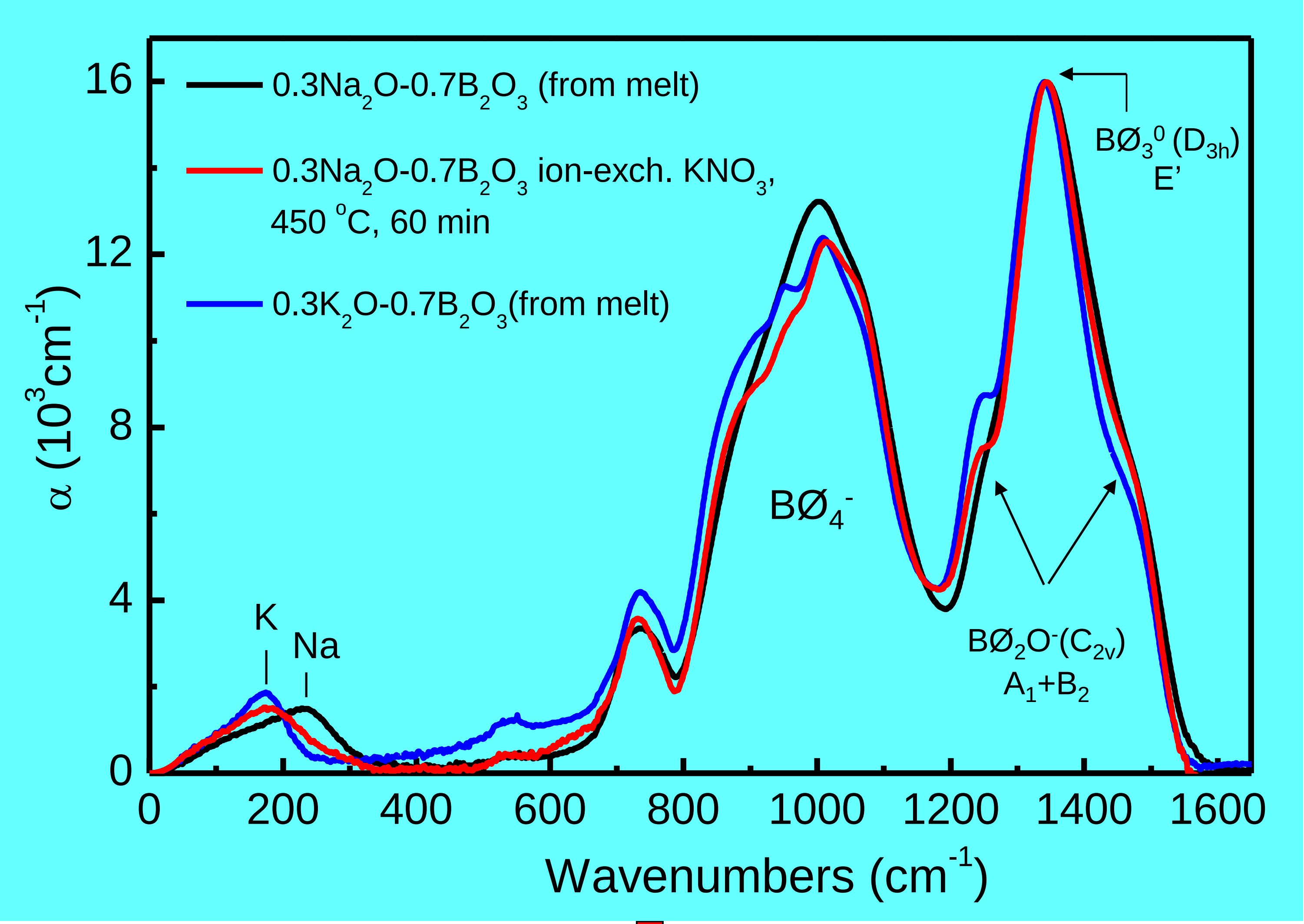
IR reflectance spectra



THERMALLY ION-EXCHANGED $0.3Na_2O-0.7B_2O_3$ GLASS: K^+/Na^+
IR absorption spectra





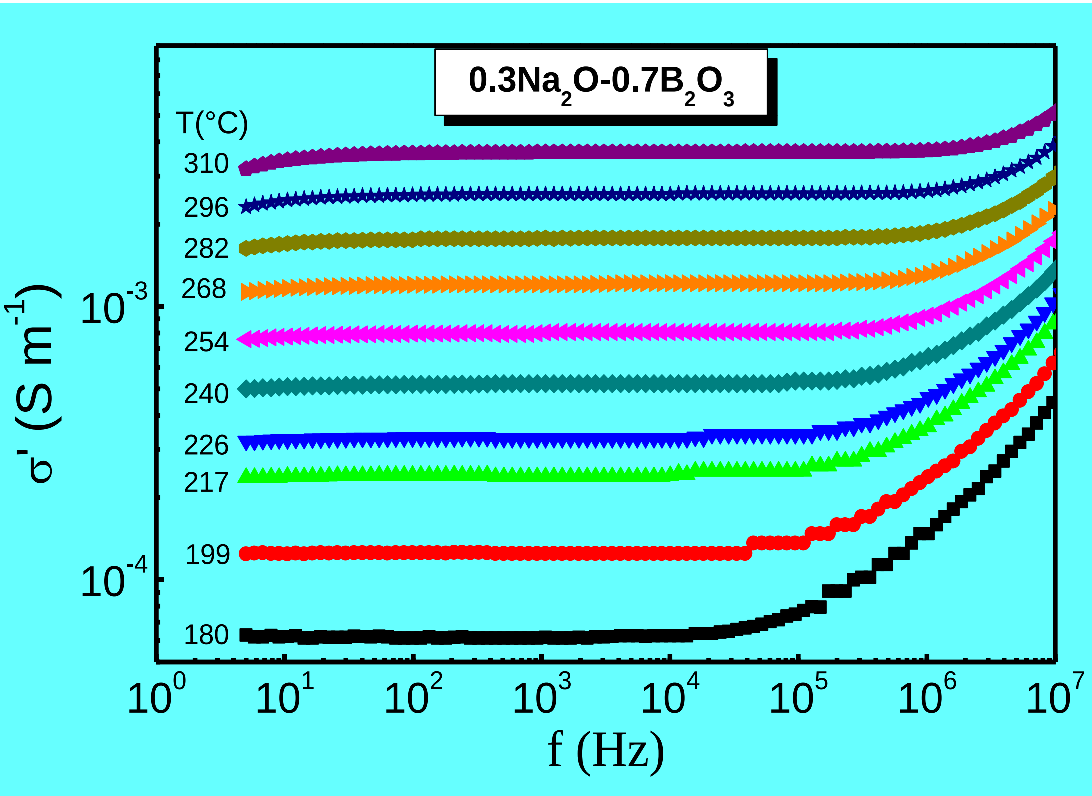


$BØ_4^- \Leftrightarrow BØ_2O^-$

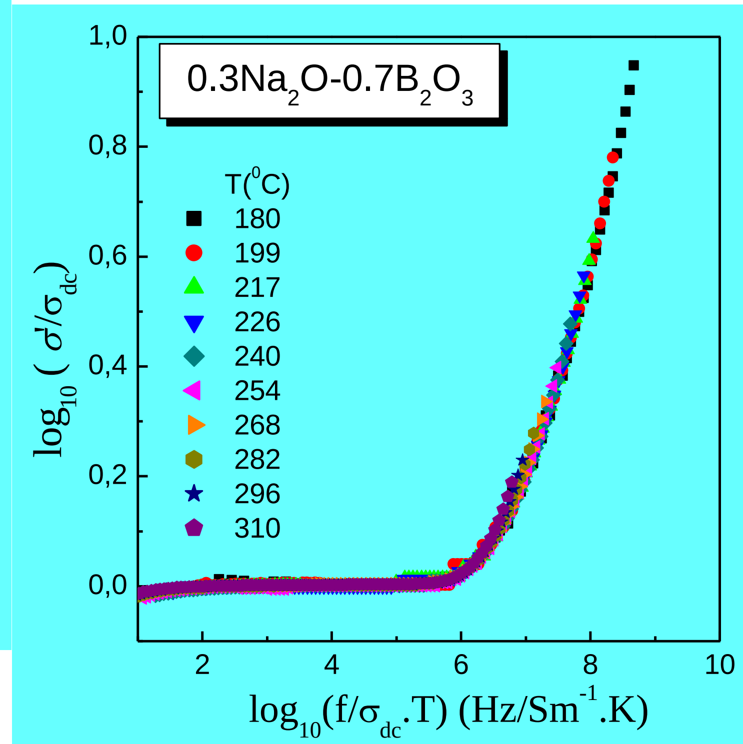
local structure rearranges

to meet the needs of K^+ ions

Conductivity spectra of the base glass: $0.3Na_2O\text{-}0.7B_2O_3$

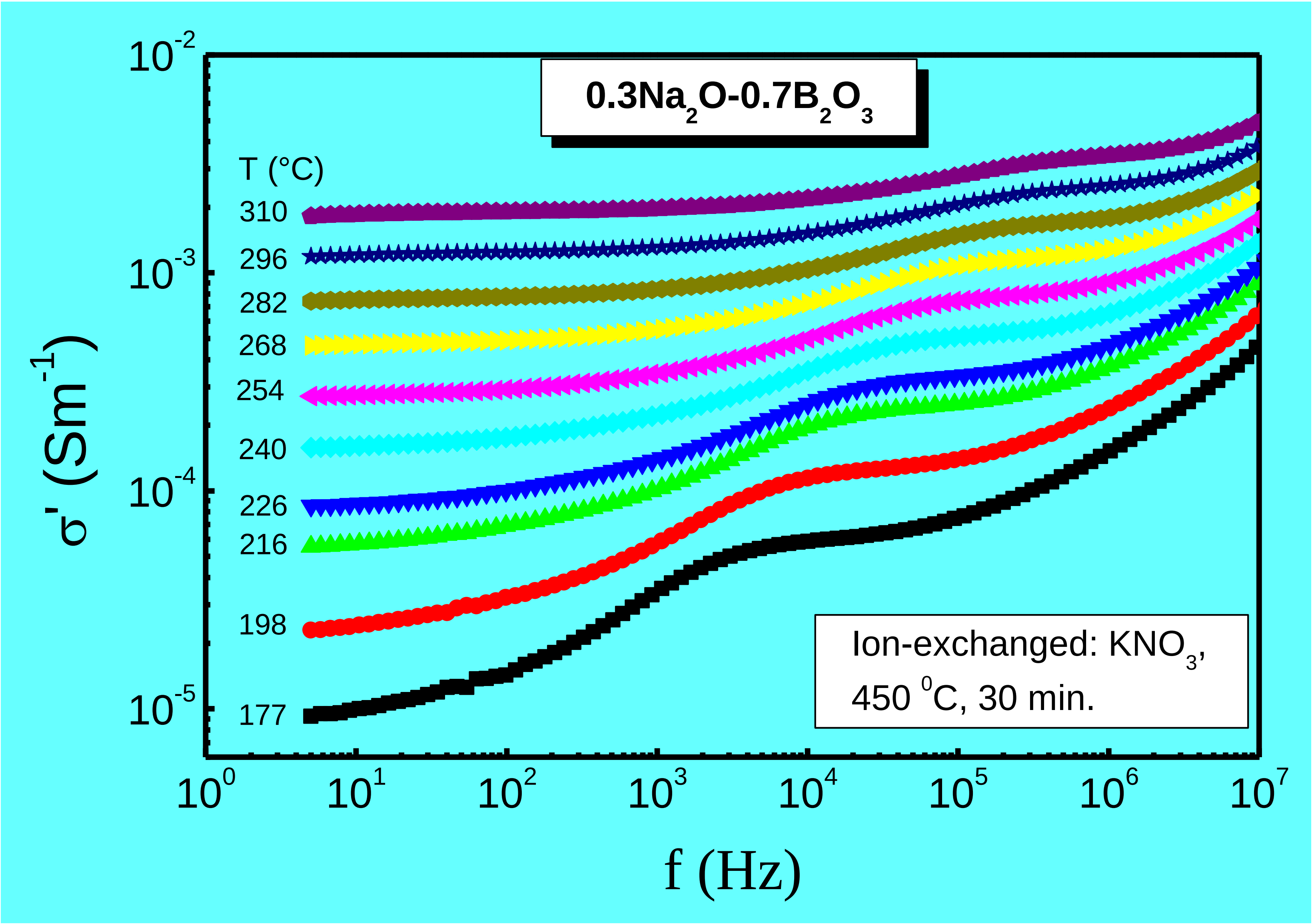


scaled conductivity spectra

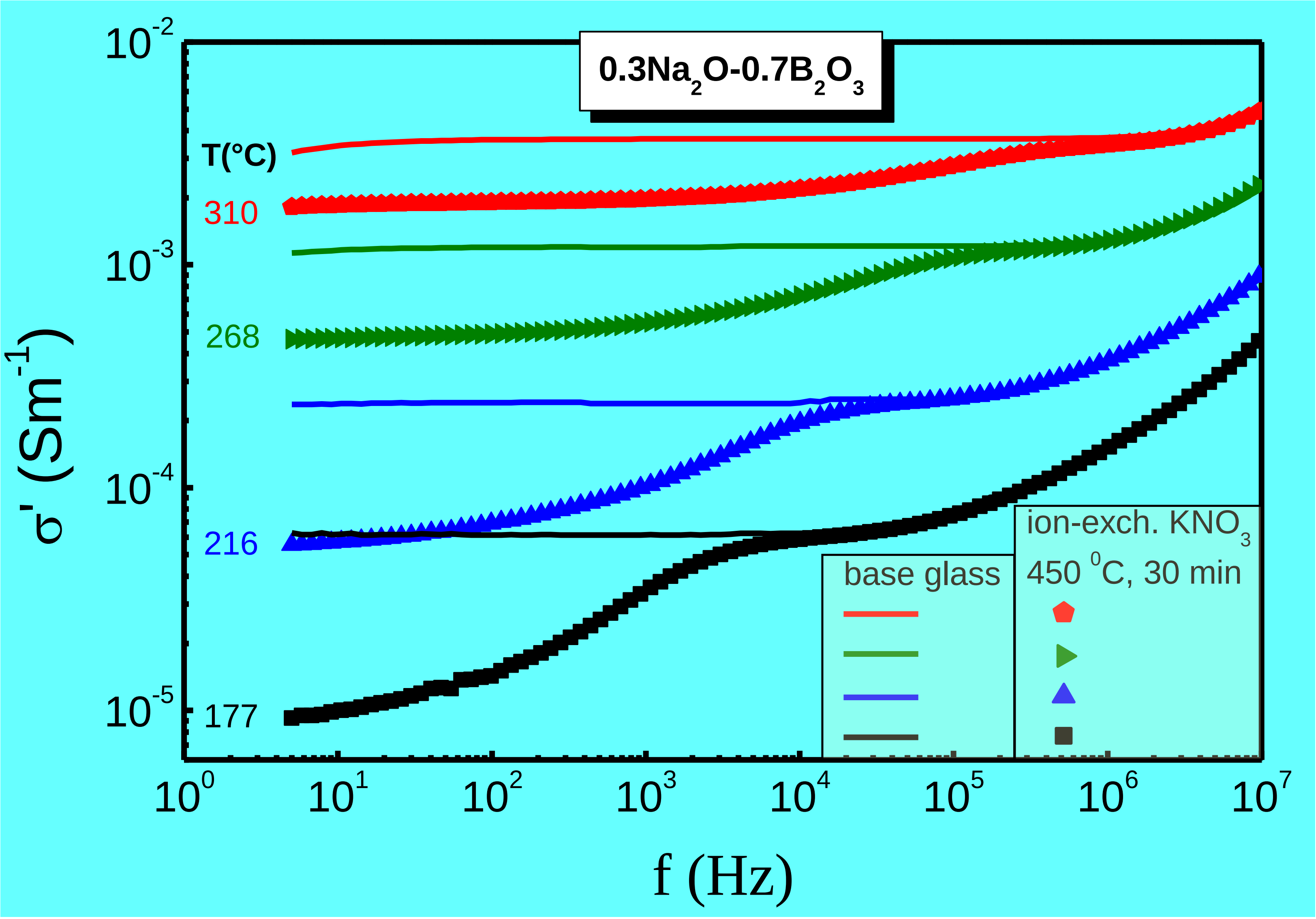


see: B. Roling, A.Happe, K. Funke & M.D. Ingram, Phys. Rev. Lett. 78 (1997) 2160.

Conductivity spectra of the $0.3Na_2O$-$0.7B_2O_3$ glass ion-exchanged in KNO_3

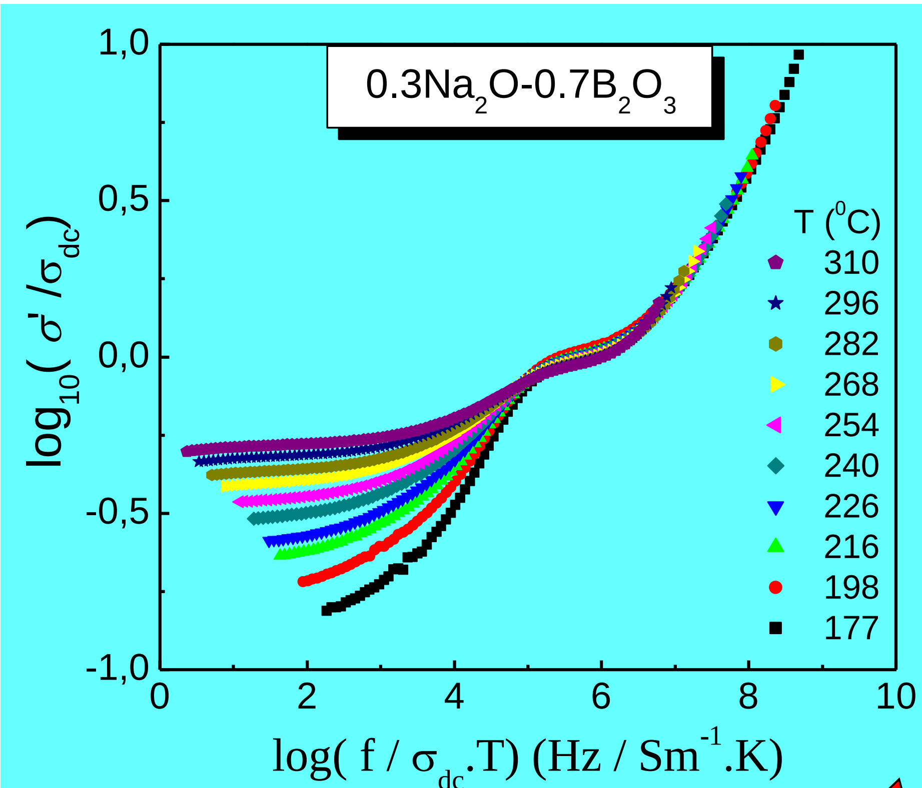


Comparison of conductivity spectra of the base glass $0.3Na_2O$-$0.7B_2O_3$ with those obtained after ion-exchange in KNO_3 at 450 ^{0}C for 30 min

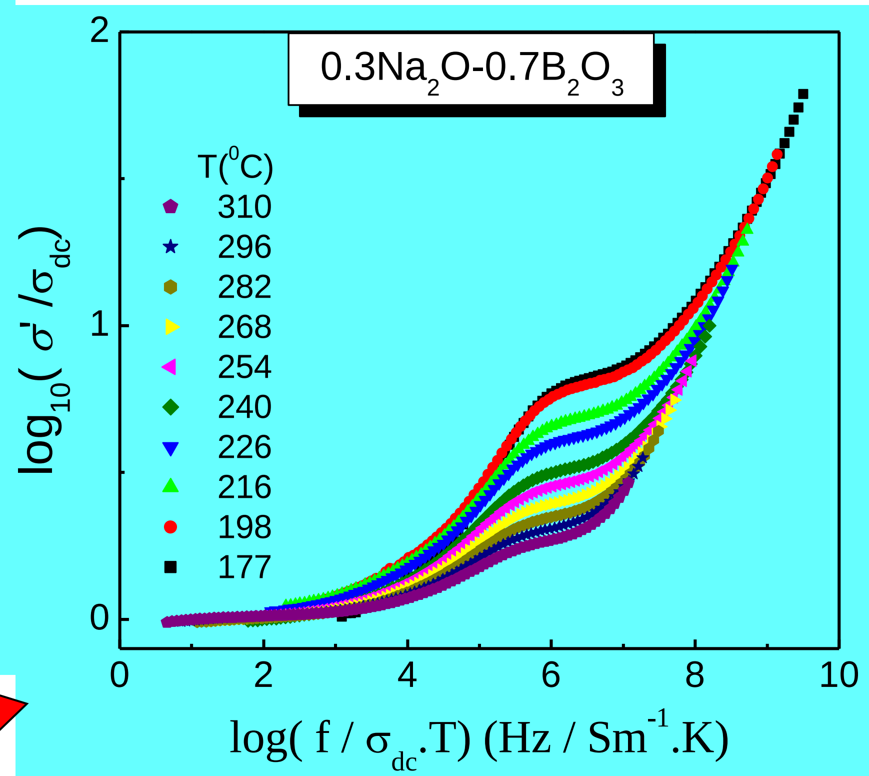


Scaled conductivity spectra of the $0.3Na_2O$-$0.7B_2O_3$ glass ion-exchanged in KNO_3 at 450 ^{0}C for 30 min

scaled with σ_{dc} of the base glass



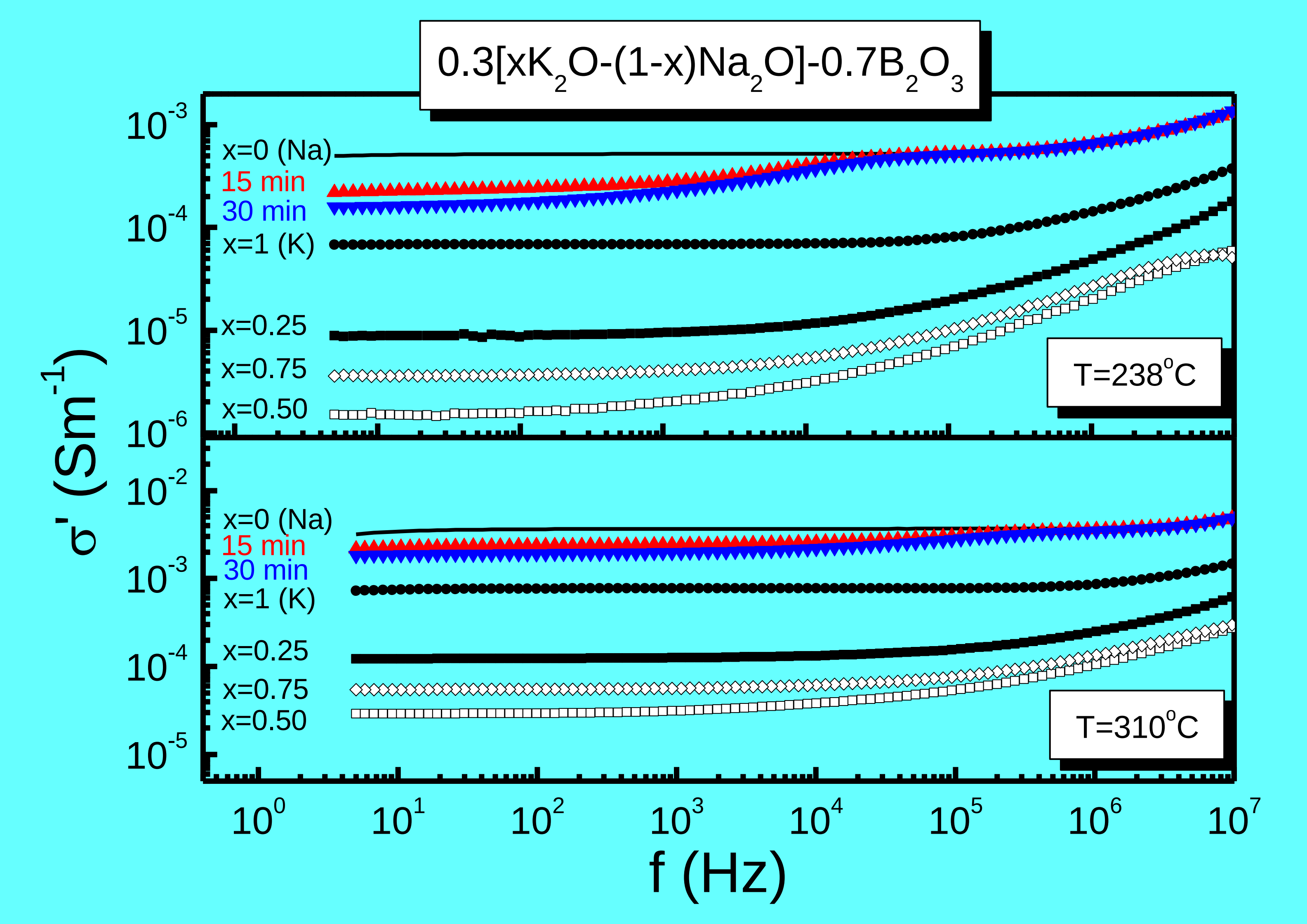
scaled with low-frequency σ_{dc} of the ion-exchanged glass



K^+/Na^+ ion exchange below T_g leads to the development of a highly resistive surface layer

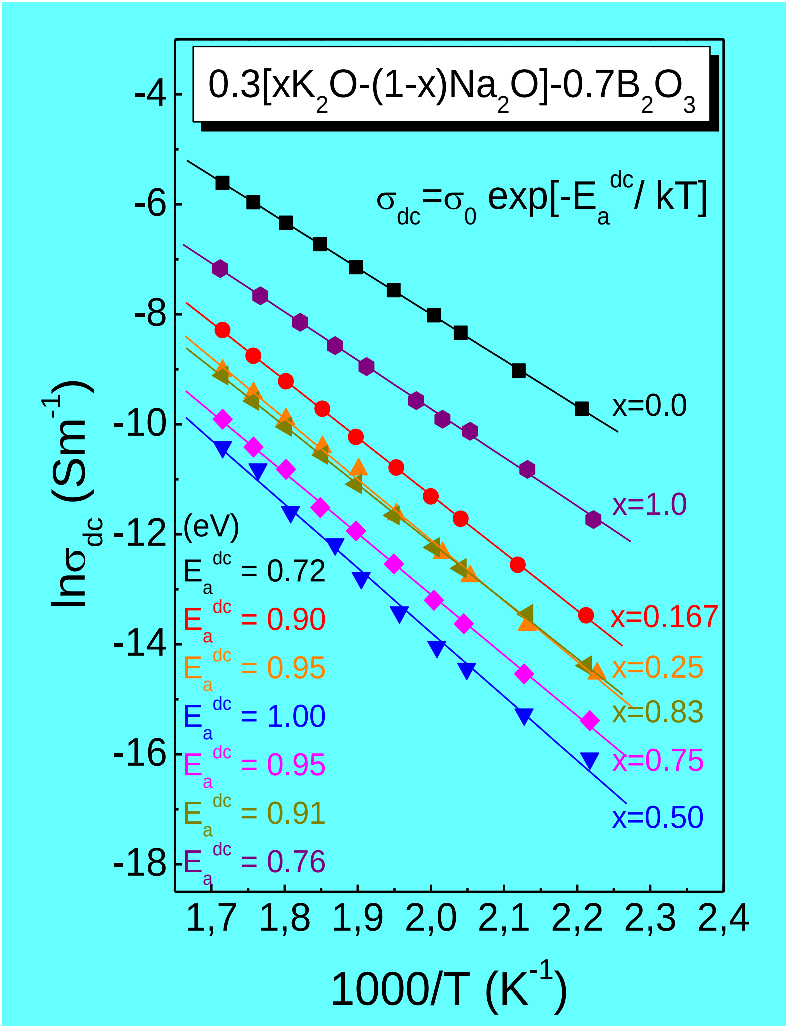
Comparison of conductivity spectra of mixed alkali glasses

$0.3[xK_2O-(1-x)Na_2O]-0.7B_2O_3$: melt-grown vs ion-exchanged glasses

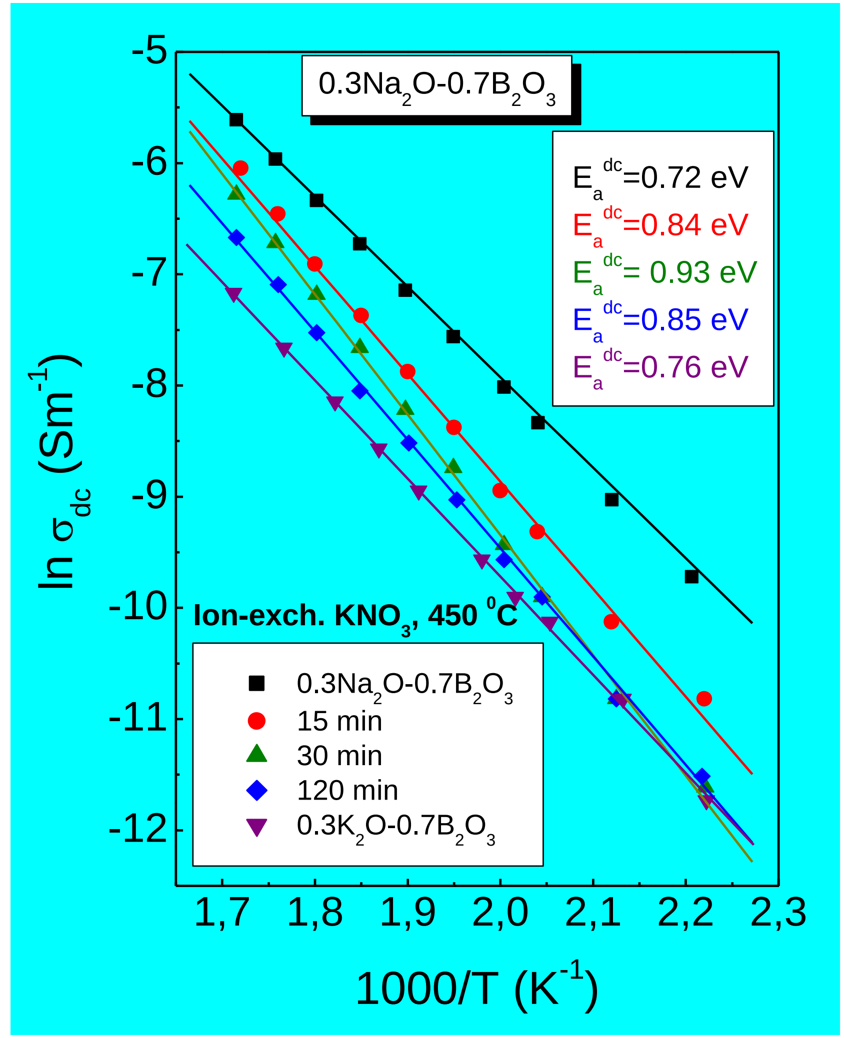


Comparison of activation energies for dc conductivity: melt-grown $0.3[xK_2O-(1-x)Na_2O]-0.7B_2O_3$ glasses vs ion-exchanged glasses

melt-grown



ion-exchanged



Dielectric spectra in the resistivity representation

Dielectric measurements: apply voltage $V(\omega)=V_m\sin(\omega t)$

measure current $I(\omega)=I_m \sin(\omega t+\delta)$

Complex impedance:

$$Z^*(\omega) = Z'(\omega) - iZ''(\omega)$$

$$Z' = |Z^*|\cos\delta, \quad Z'' = |Z^*|\sin\delta, \quad |Z^*| = \frac{V_m}{I_m}$$

Complex resistivity:

$$\rho^*(\omega) = \rho'(\omega) - i\rho''(\omega) = Z^*(\omega)\,\frac{S}{d}$$

d=sample thickness; *S*=electrode area

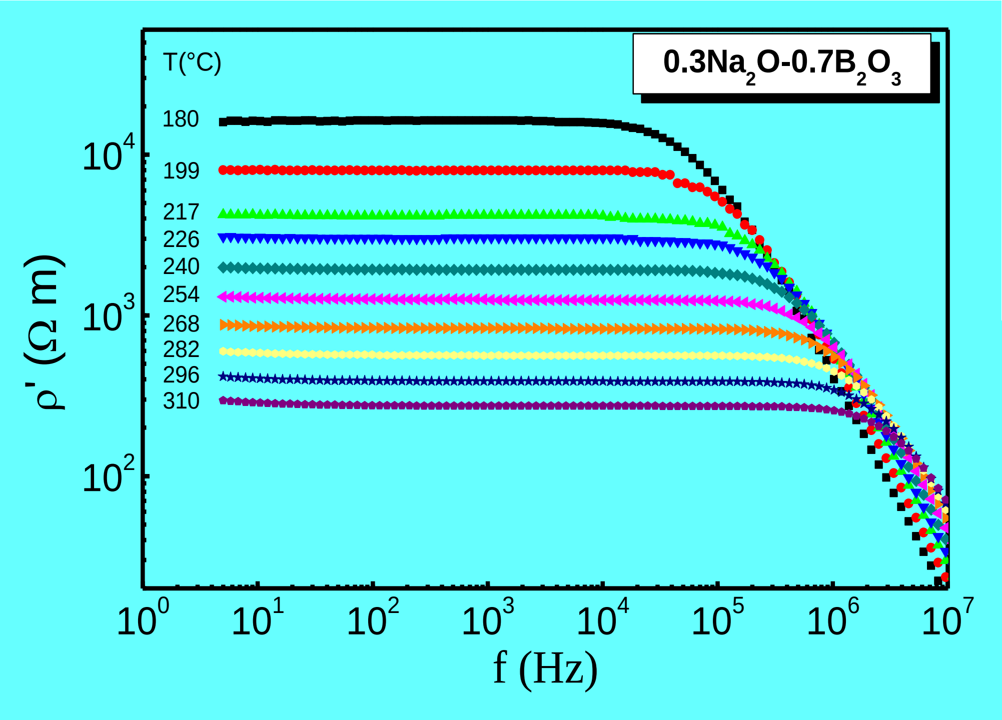
Complex conductivity:

$$\sigma^*(\omega) = \sigma'(\omega) + i\sigma''(\omega) = \frac{1}{\rho^*(\omega)}$$

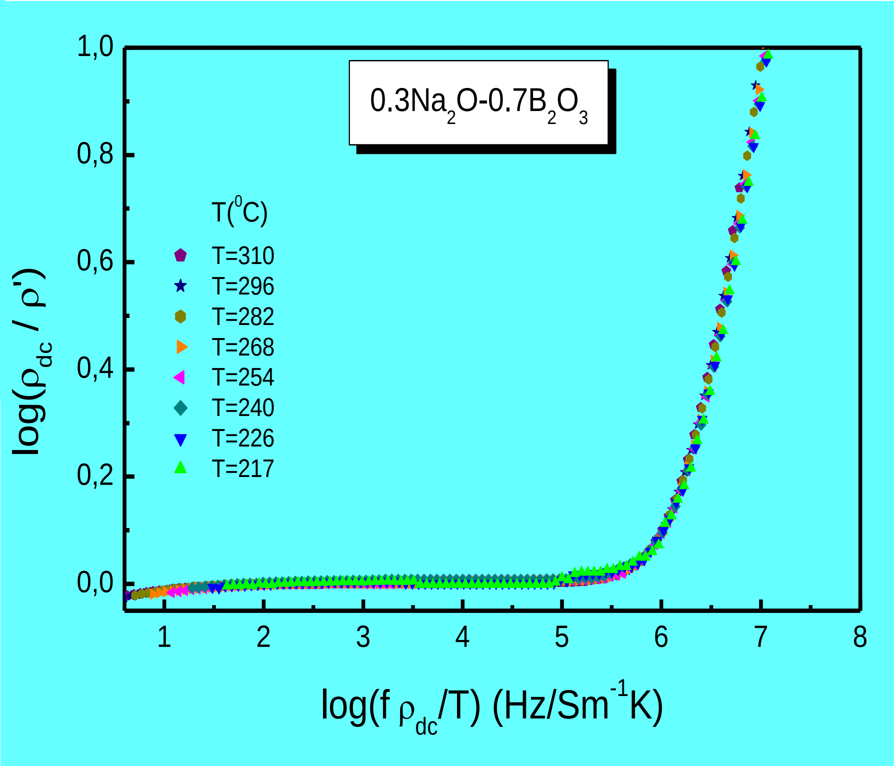
$$\sigma'(\omega) = \frac{\rho'(\omega)}{[\rho'(\omega)]^2 + [\rho''(\omega)]^2}$$

$$\rho'(\omega) = \frac{\sigma'(\omega)}{[\sigma'(\omega)]^2 + [\sigma''(\omega)]^2}$$

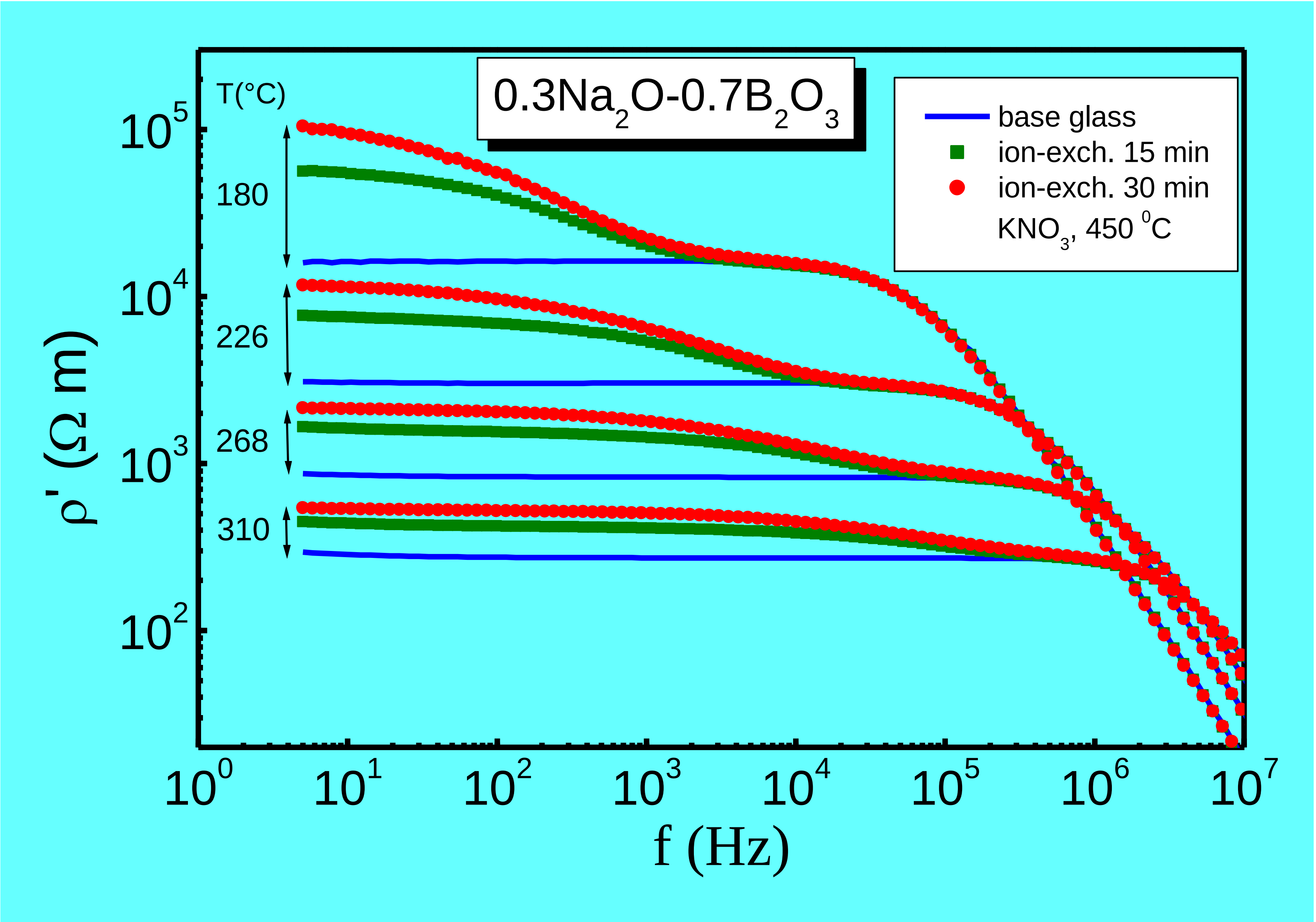
Resistivity spectra of the base glass: $0.3Na_2O-0.7B_2O_3$



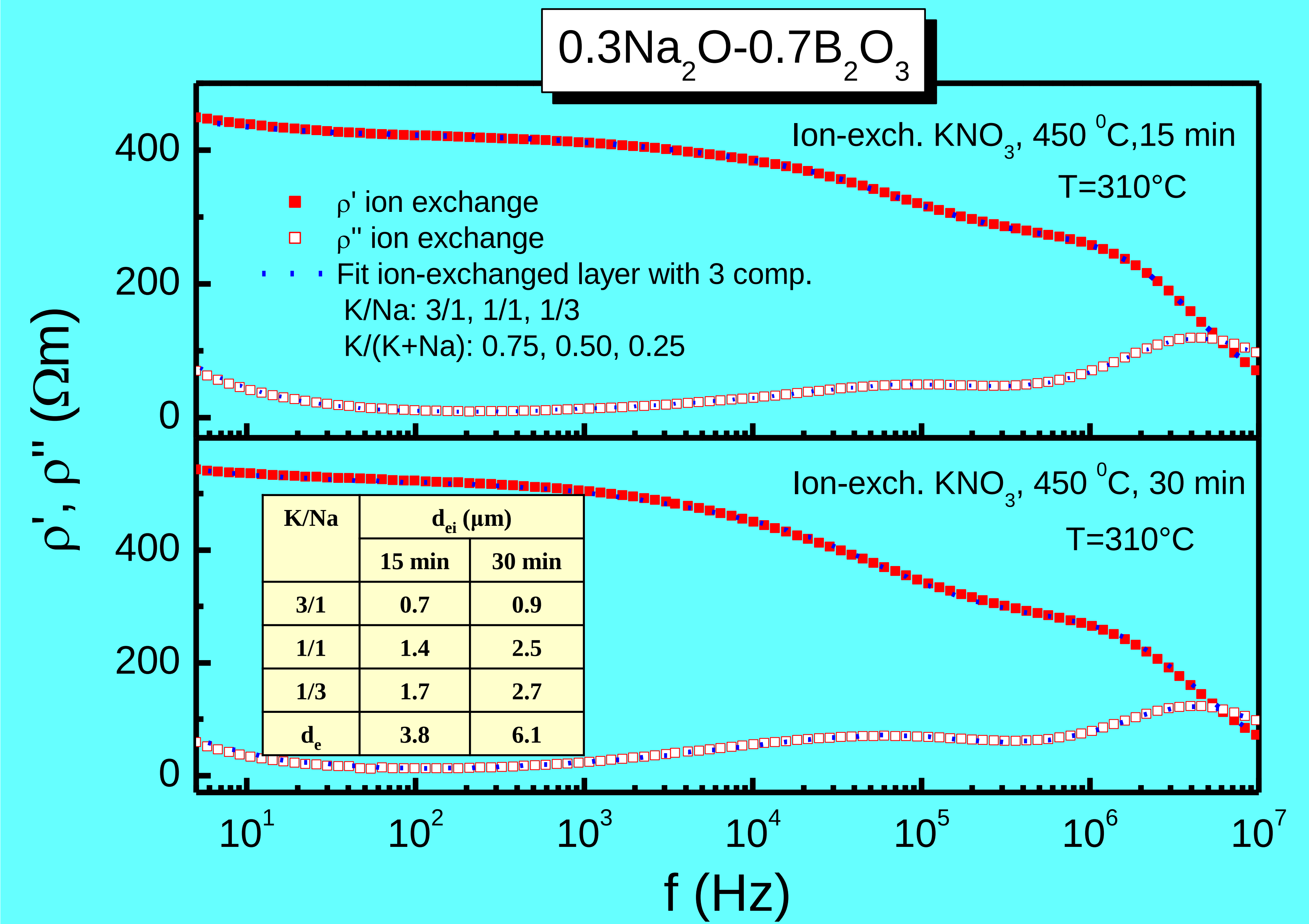
scaled resistivity spectra



Resistivity spectra of the $0.3Na_2O$-$0.7B_2O_3$ glass ion-exchanged in KNO_3

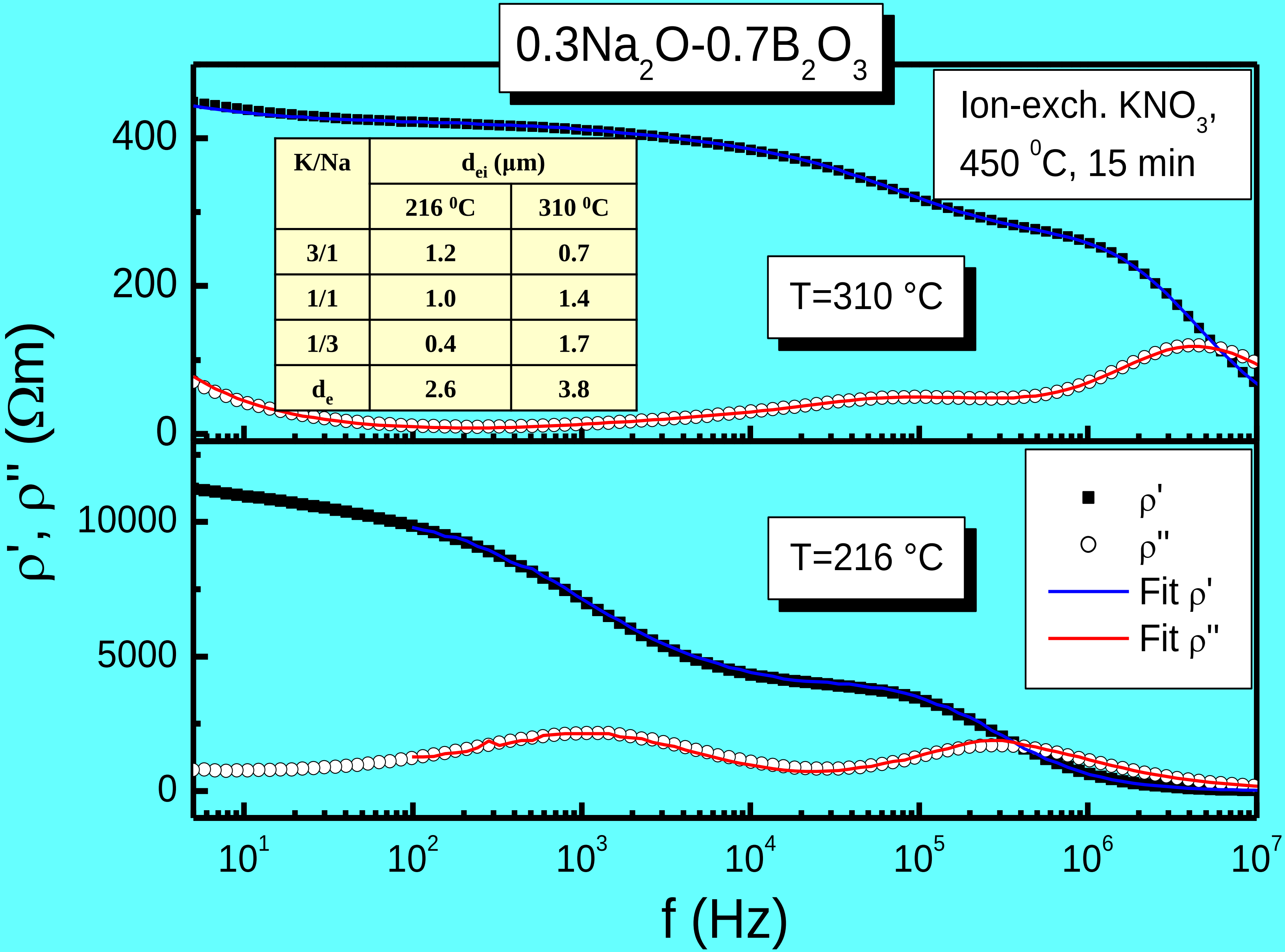


Resistivity spectra of the $0.3Na_2O$-$0.7B_2O_3$ glass ion-exchanged in KNO_3



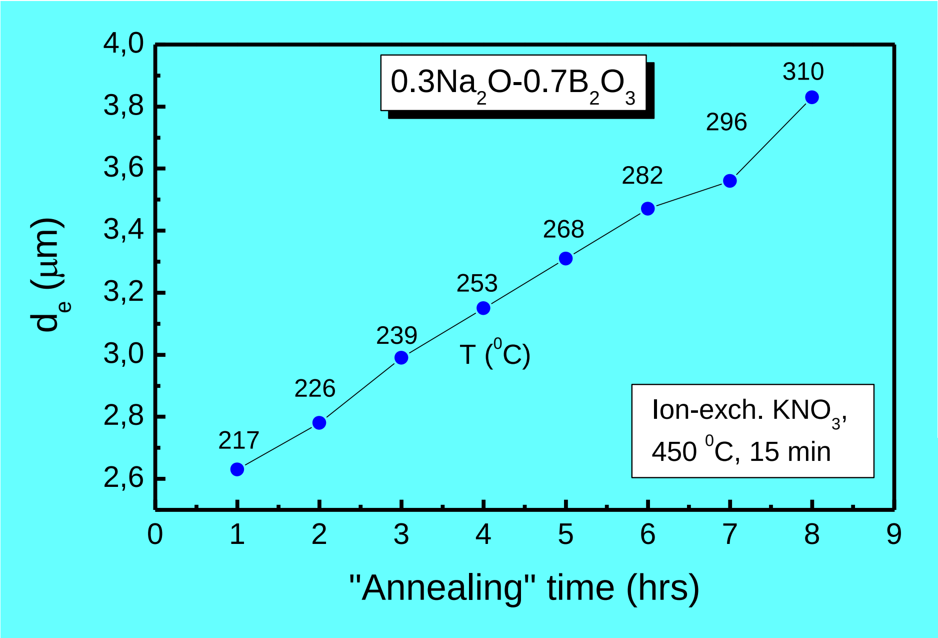
K/Na	d_{ei} (μm)	
	15 min	30 min
3/1	0.7	0.9
1/1	1.4	2.5
1/3	1.7	2.7
d_e	3.8	6.1

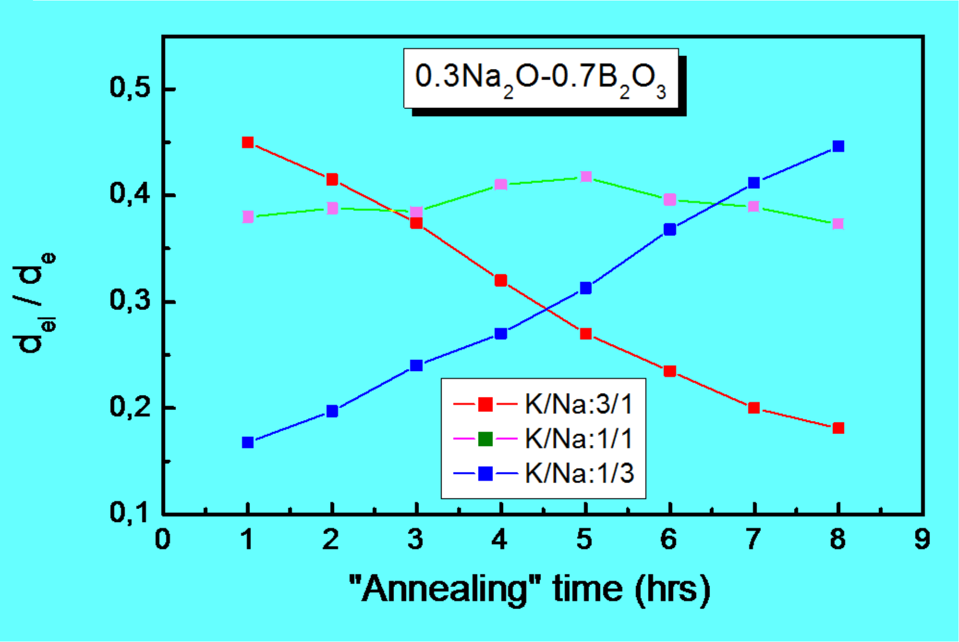
"Annealing" of the $0.3Na_2O$-$0.7B_2O_3$ ion-exchanged glass



K/Na	d_{ei} (μm)	
	216 ^{0}C	310 ^{0}C
3/1	1.2	0.7
1/1	1.0	1.4
1/3	0.4	1.7
d_e	2.6	3.8

“Annealing” of the $0.3Na_2O$-$0.7B_2O_3$ ion-exchanged glass, cont.





SUMMARY

- **Structural aspects of ion-exchanged glasses: soda-lime-silica & sodium-borate**

⇒ Alkali ion motion in the glass matrix below T_g, caused either by ion exchange and/or annealing, is accompanied by local structural rearrangements/relaxations involving short-range order structural units (Cation Induced Relaxations Of the Network, CIRON).

⇒ The structural rearrangements depend on the nature of the glass network and the type of the foreign cation introduced into the glass structure:

Soda-lime-silica glass:

K^+/Na^+: $Q^2 + Q^4 \Rightarrow 2Q^3$
Li^+, Ag^+/Na^+: $2Q^3 \Rightarrow Q^2 + Q^4$

Sodium-borate glass:

K^+/Na^+: $BØ_4^- \Rightarrow BØ_2O^-$

⇒ The structure of an ion-exchanged glass resembles that of the corresponding melt-grown mixed alkali glass (i.e. similar SRO structure and nature of sites hosting metal ions).

SUMMARY cont.

- **Ac conductivity aspects of ion-exchanged glasses: sodium-borate glass**

⇒ The resistivity of the ion-exchanged (surface) layer can be described in terms of the resistivities of melt-grown K/Na mixed alkali glasses.

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⇒ Royal Society / NHRF (exchange program)

⇒ General Secretariat for Research and Technology / Ministry of Development in Greece

⇒ European Union (project HPMD-CT-2000-00033).