

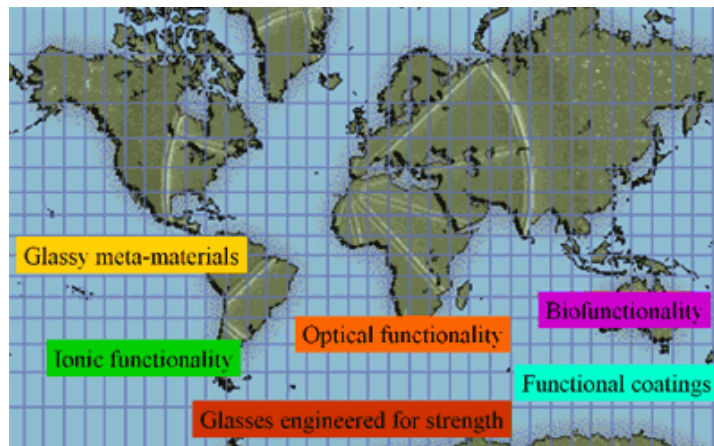


Structure and dynamics of ion-exchanged glasses

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National Hellenic Research Foundation, Athens, Greece*

**17th University Conference on Glass Science
&
1st International Materials Institute Workshop on
NEW FUNCTIONALITY IN GLASSES**

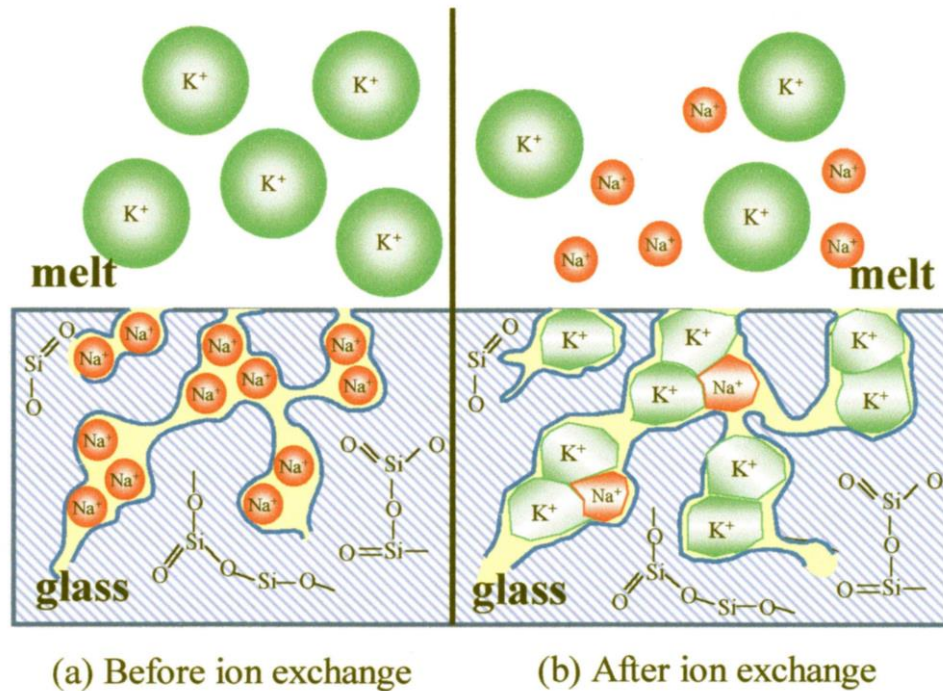


June 26-30, 2005 / State College, Pennsylvania

Outline of presentation

- Ion-exchange process: introduction & relevant literature
- Structure of ion-exchanged soda-lime-silica glass
- Structure of ion-exchanged $30\text{Na}_2\text{O}-70\text{B}_2\text{O}_3$ glass
- ac conductivity spectra of ion-exchanged $30\text{Na}_2\text{O}-70\text{B}_2\text{O}_3$ glass
- Summary

ION EXCHANGE PROCESS IN GLASS



ion “crowding”



compressive stress



permanent compression

$T < T_g$

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

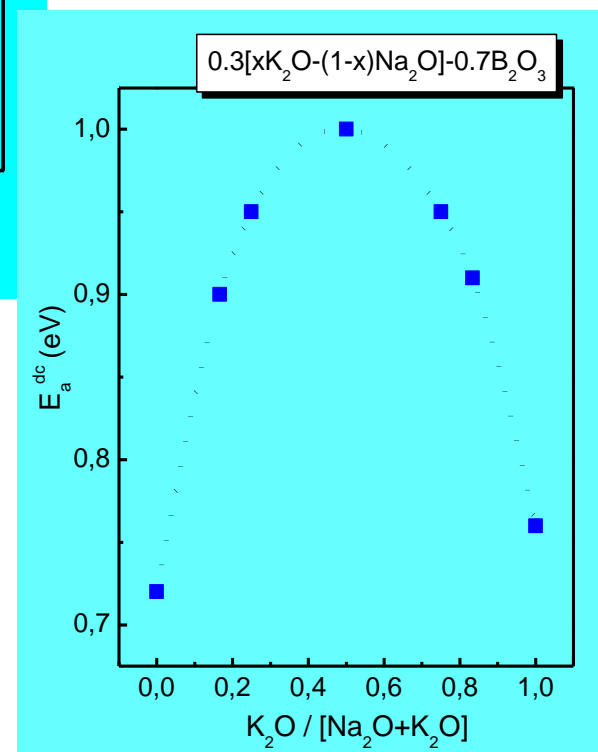
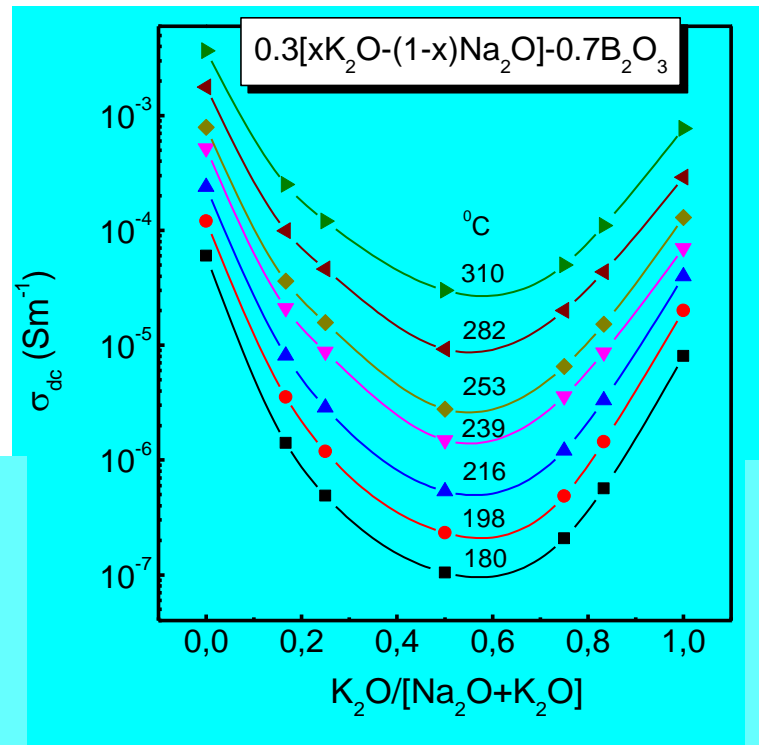
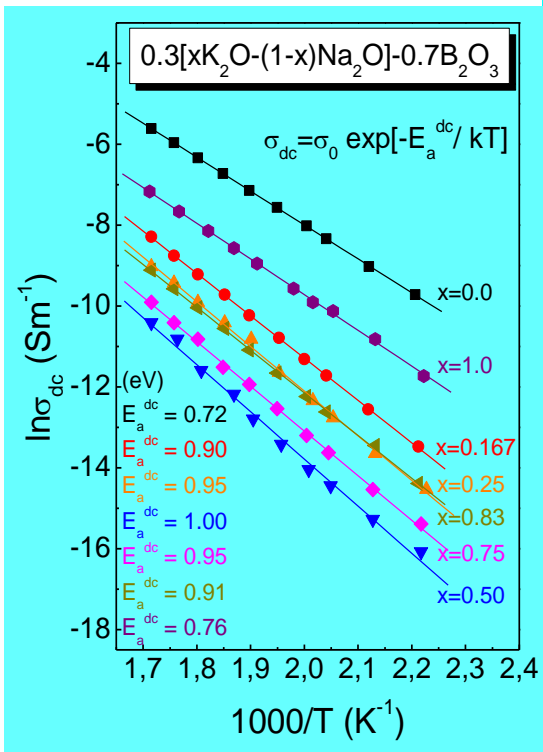
Applications:

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

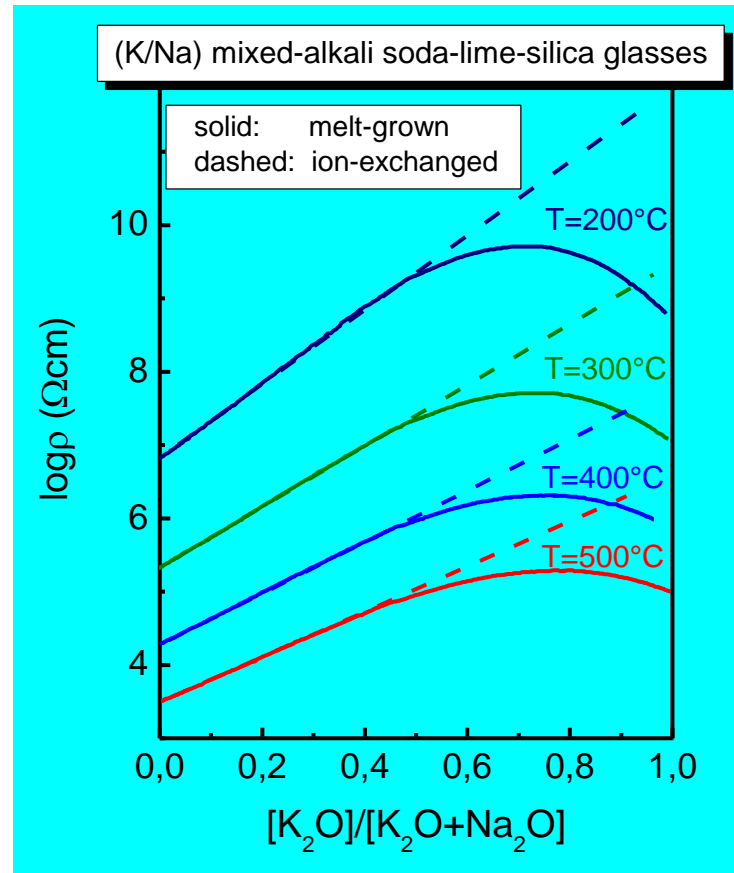
Open Questions:

- 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 $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-2\text{SiO}_2$ 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 $\text{Na}_2\text{O}-4\text{SiO}_2$ glasses / X-ray absorption fine structure (XAFS)

⇒ CN (Na/O) ≈ 5 , $r(\text{Na}-\text{O})=2.30-2.32 \text{ \AA}$

⇒ CN (Ag/O) ≈ 2 , $r(\text{Ag}-\text{O})=2.08-2.23 \text{ \AA}$ (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 $\text{Na}_2\text{O}-2\text{SiO}_2$ 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 ($T_g=558\text{ }^\circ\text{C}$) (FGS0)	Soft glass tubing (T0)
SiO ₂	71.78	71.62
Na ₂ O	12.44	14.02
CaO	8.76	6.19
K ₂ O	0.38	1.03
MgO	5.88	4.82
BaO	none	1.50
Al ₂ O ₃	0.58	1.49
Fe ₂ O ₃	0.04	0.02
SO ₃	0.14	0.22

B. Sodium-Borate Glass: 30Na₂O-70B₂O₃ ($T_g=477\text{ }^\circ\text{C}$)

INFRARED SPECTRAL MEASUREMENTS:

- Specular reflectance at quasinormal incidence (11°)

⇒ use the same sample for continuous data acquisition in the mid- & far-IR range (25-5,000 cm⁻¹)

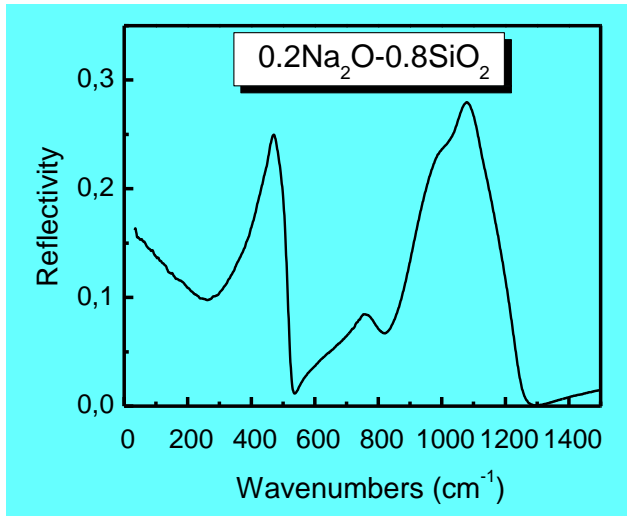
IMPEDANCE MEASUREMENTS:

- 5Hz -10MHz, f(T)

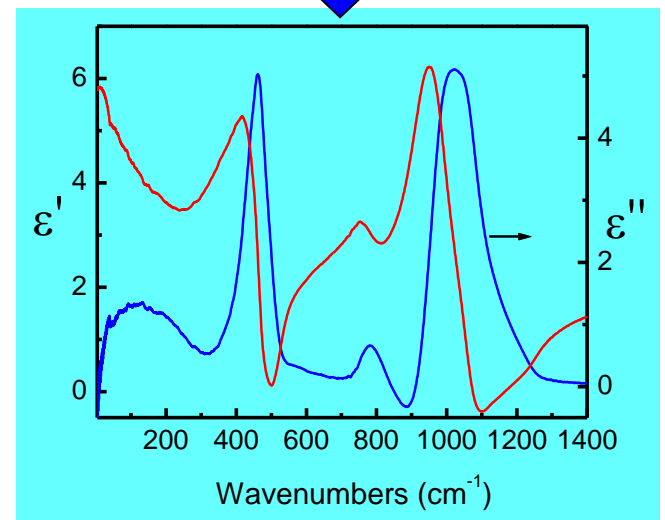
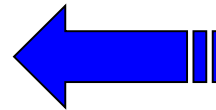
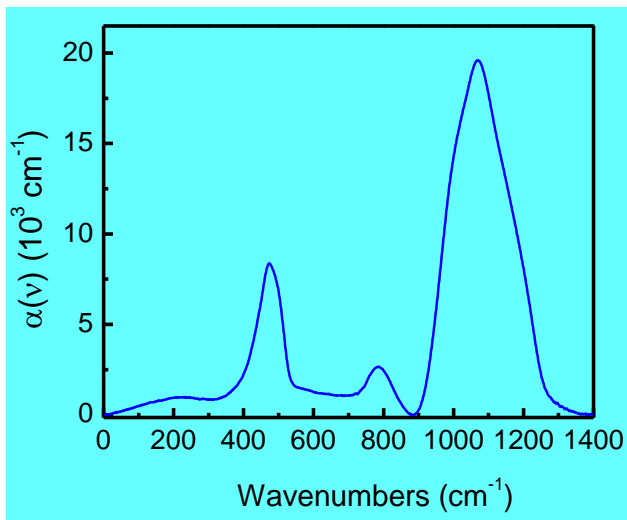
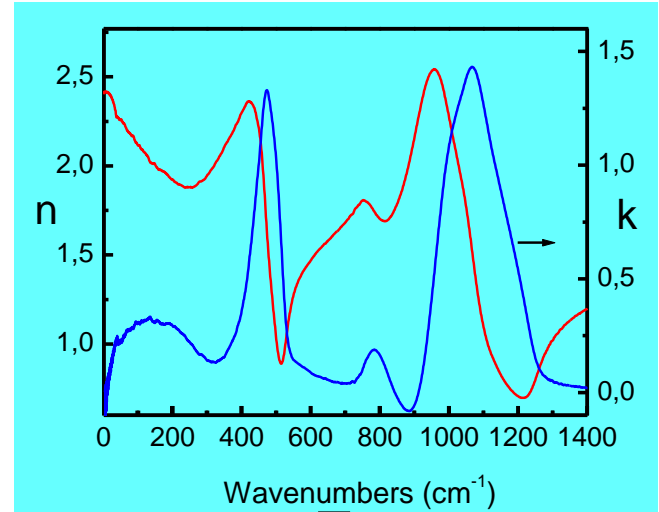
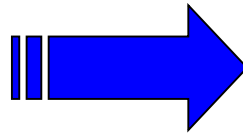
ELECTRON MICROPROBE ANALYSIS:

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

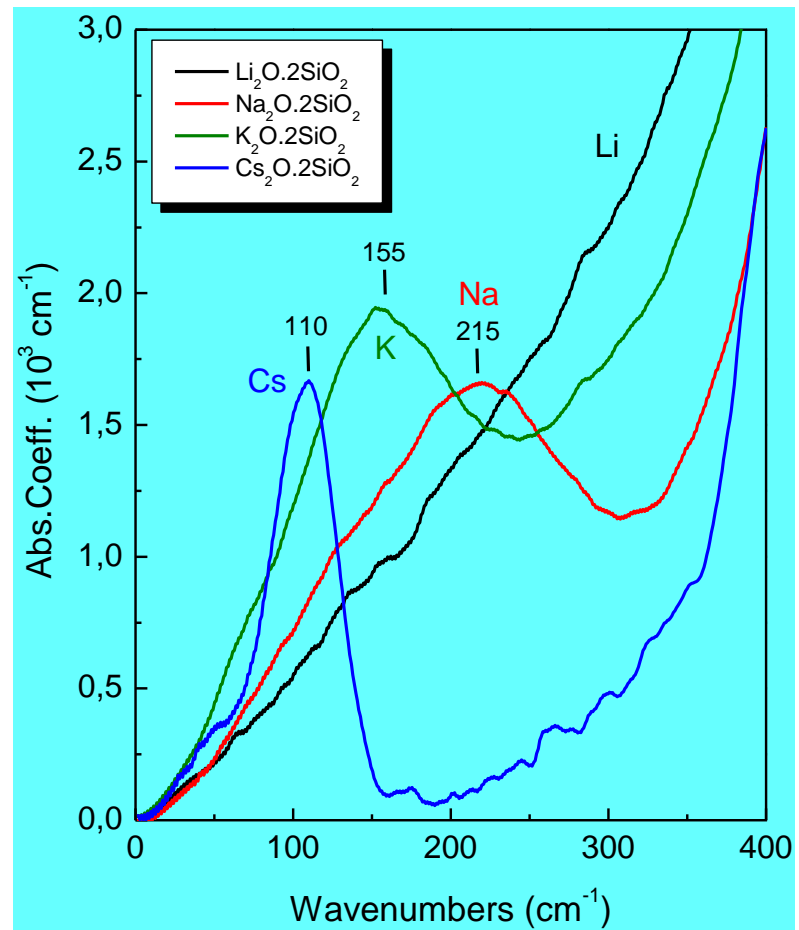
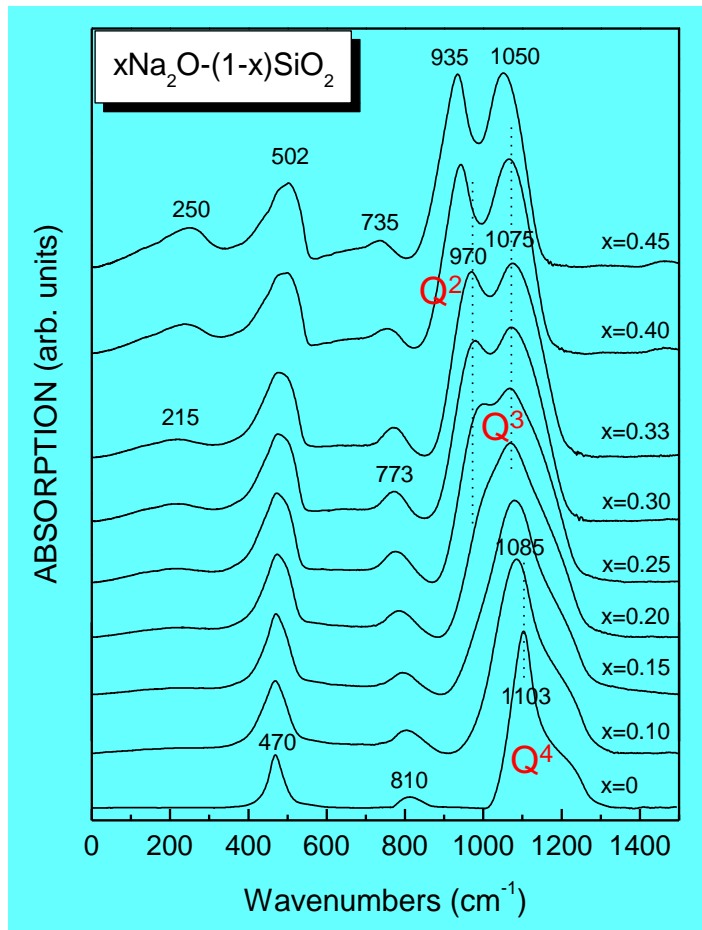
ANALYSIS OF REFLECTIVITY SPECTRA



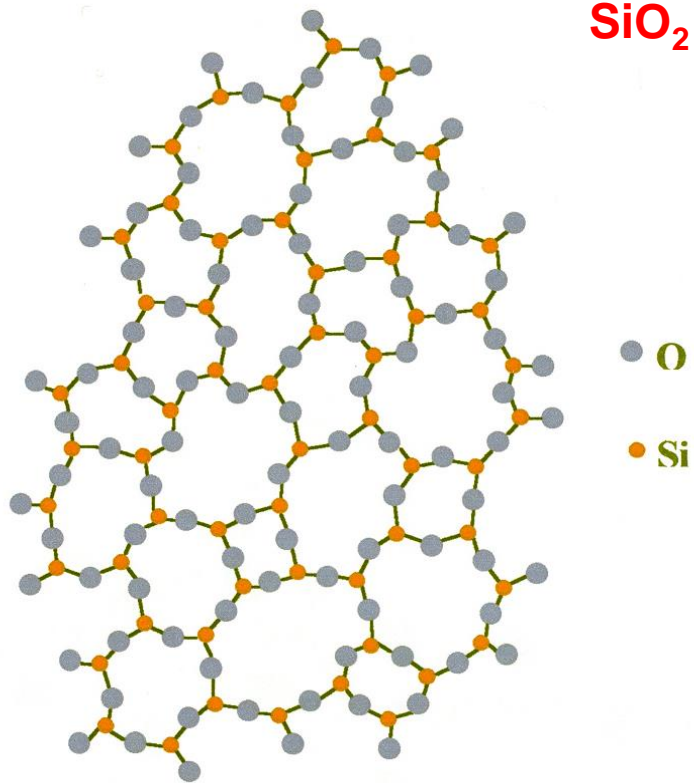
**Kramers – Kronig
transformation**



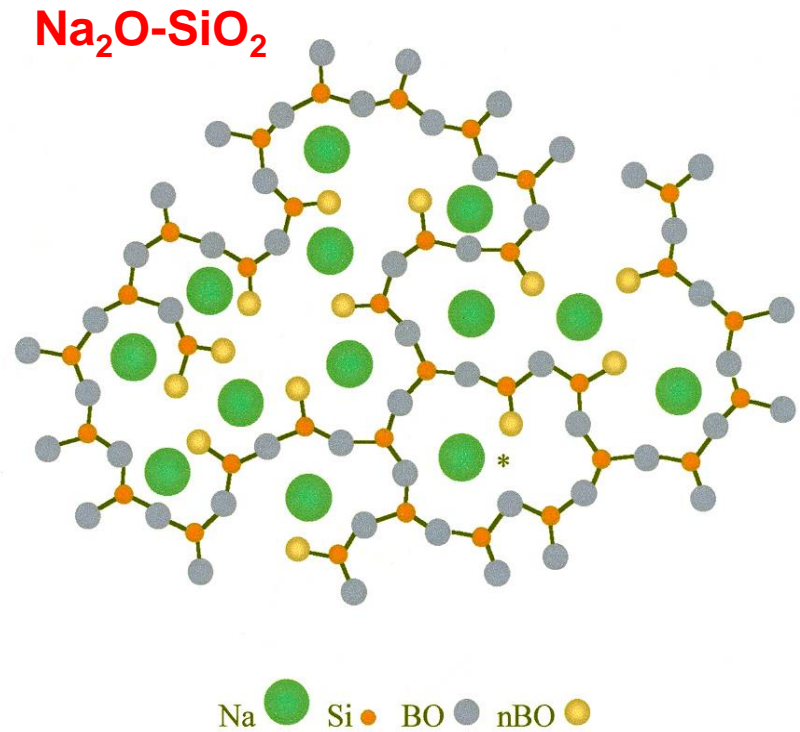
Short-range order structure and metal ion-site vibrations in silicate glasses



Continuous Random Network (CRN) Model

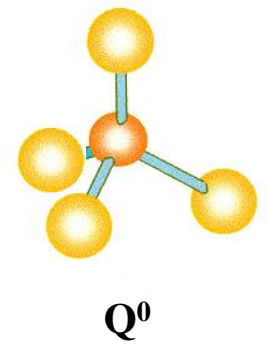
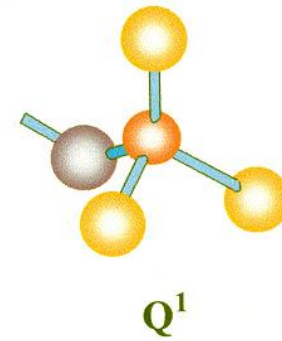
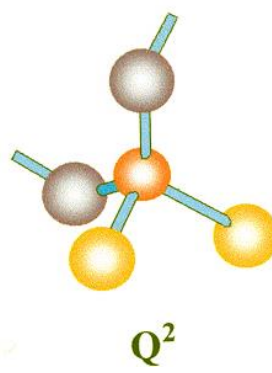
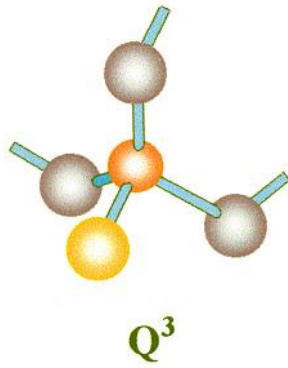
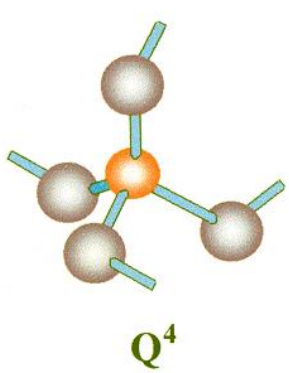


Zachariasen, 1932

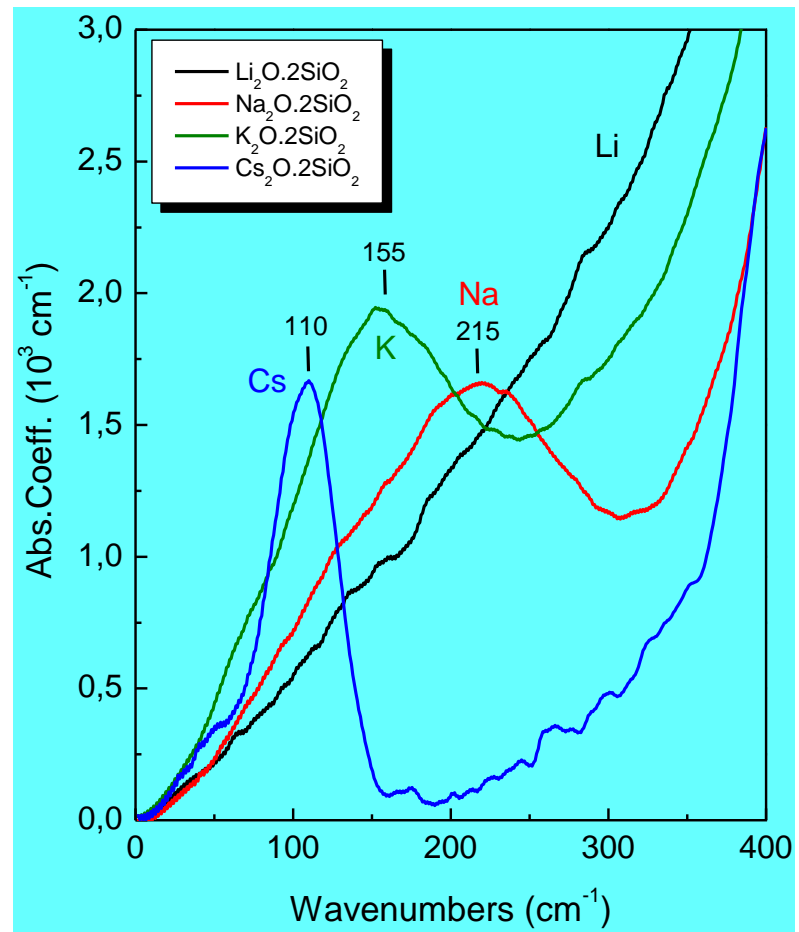
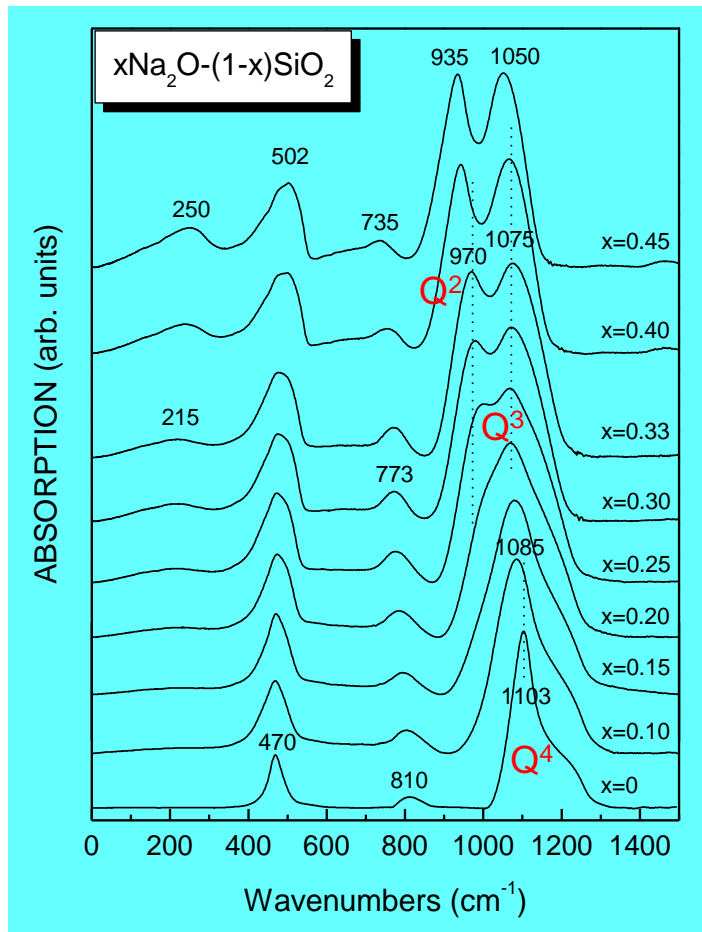


Warren-Biscoe, 1938

Q^n tetrahedral units in silicate glasses

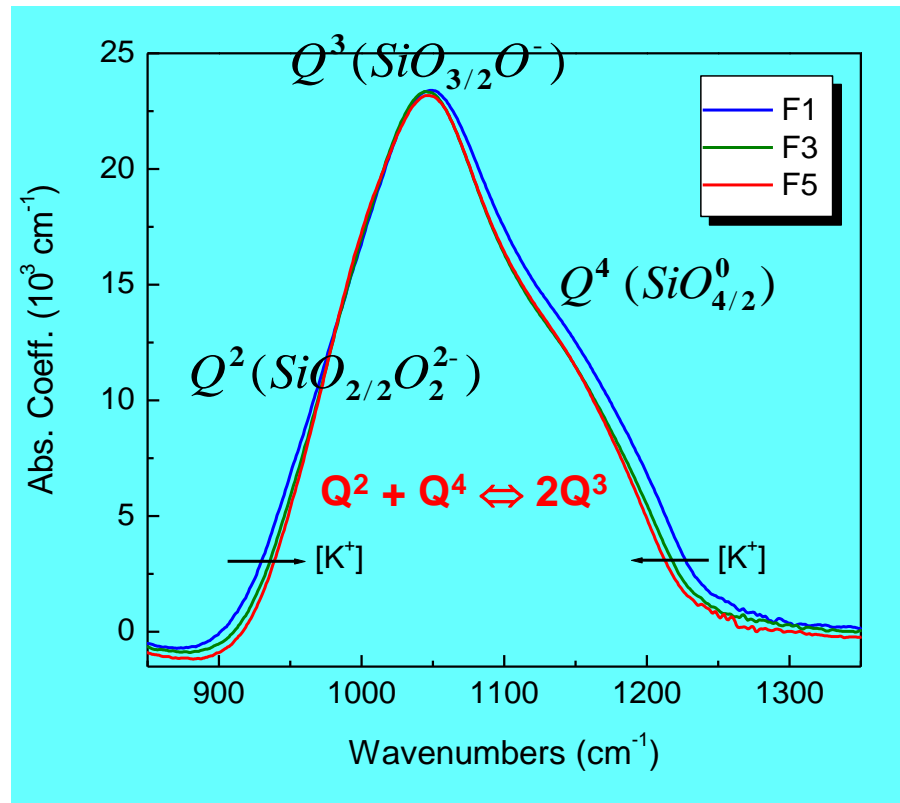
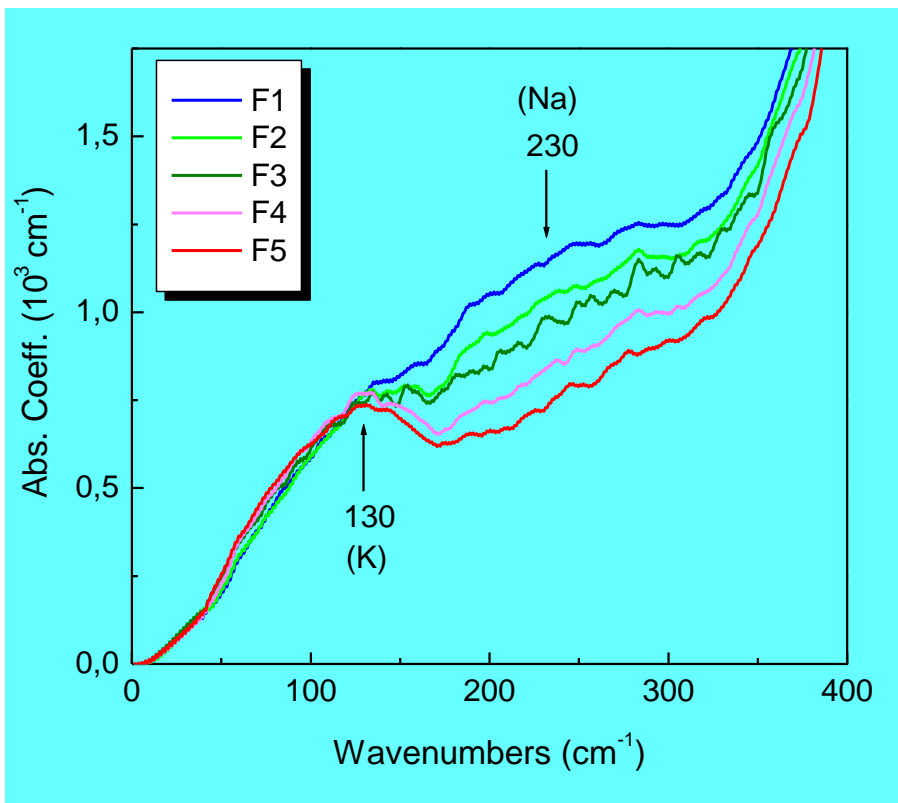


Short-range order structure and metal ion-site vibrations in silicate glasses

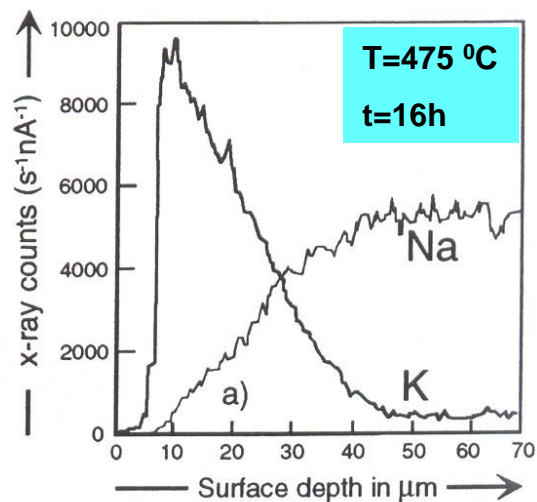
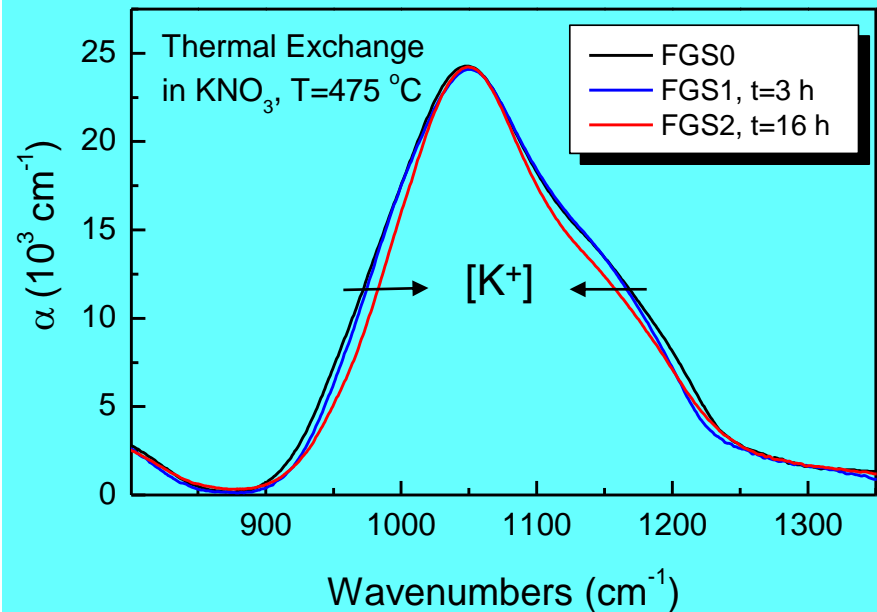
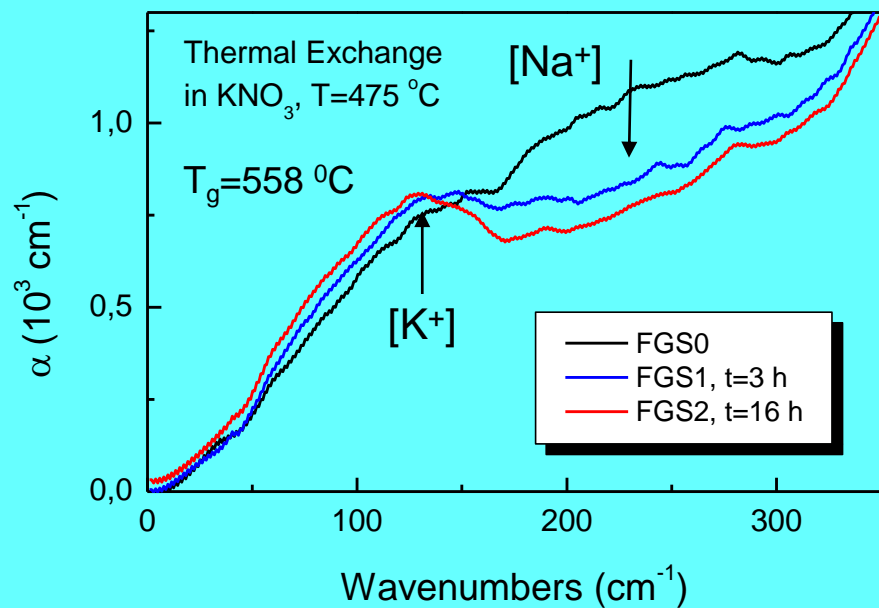


IR SPECTRA OF "SYNTHETIC" MIXED-CATION (Na⁺/K⁺) FLOAT GLASSES

"Synthetic" float glasses					
mol%	F1	F2	F3	F4	F5
Na ₂ O	12.44	9.61	6.41	3.21	0.38
K ₂ O	0.38	3.21	6.41	9.61	12.44



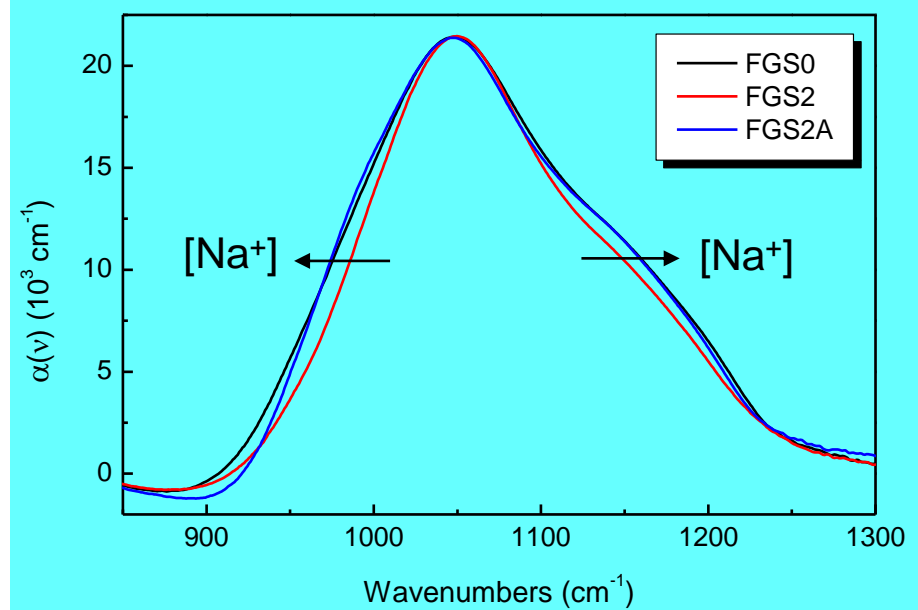
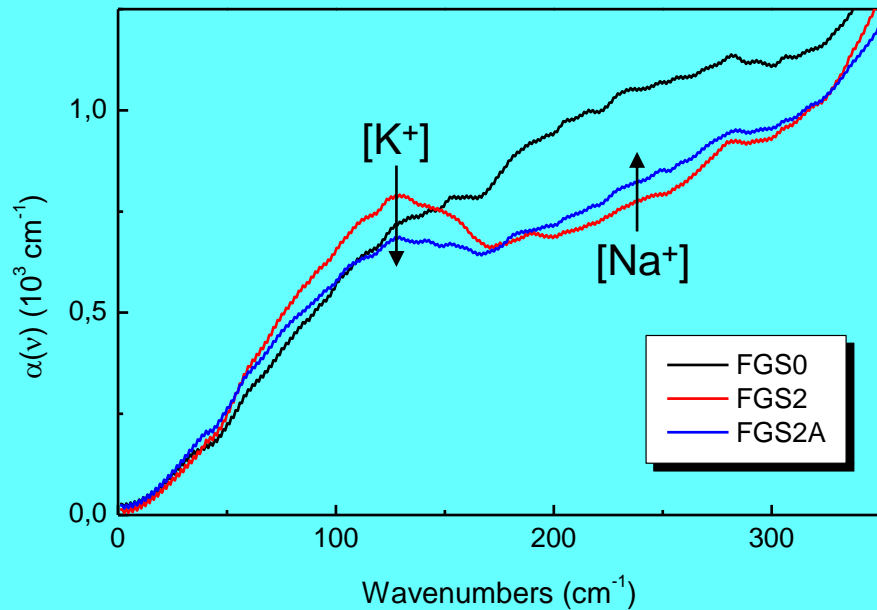
THERMALLY ION-EXCHANGED FLOAT GLASS: K⁺/Na⁺



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

glass structure becomes more homogeneous

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



FGS0: pristine float glass

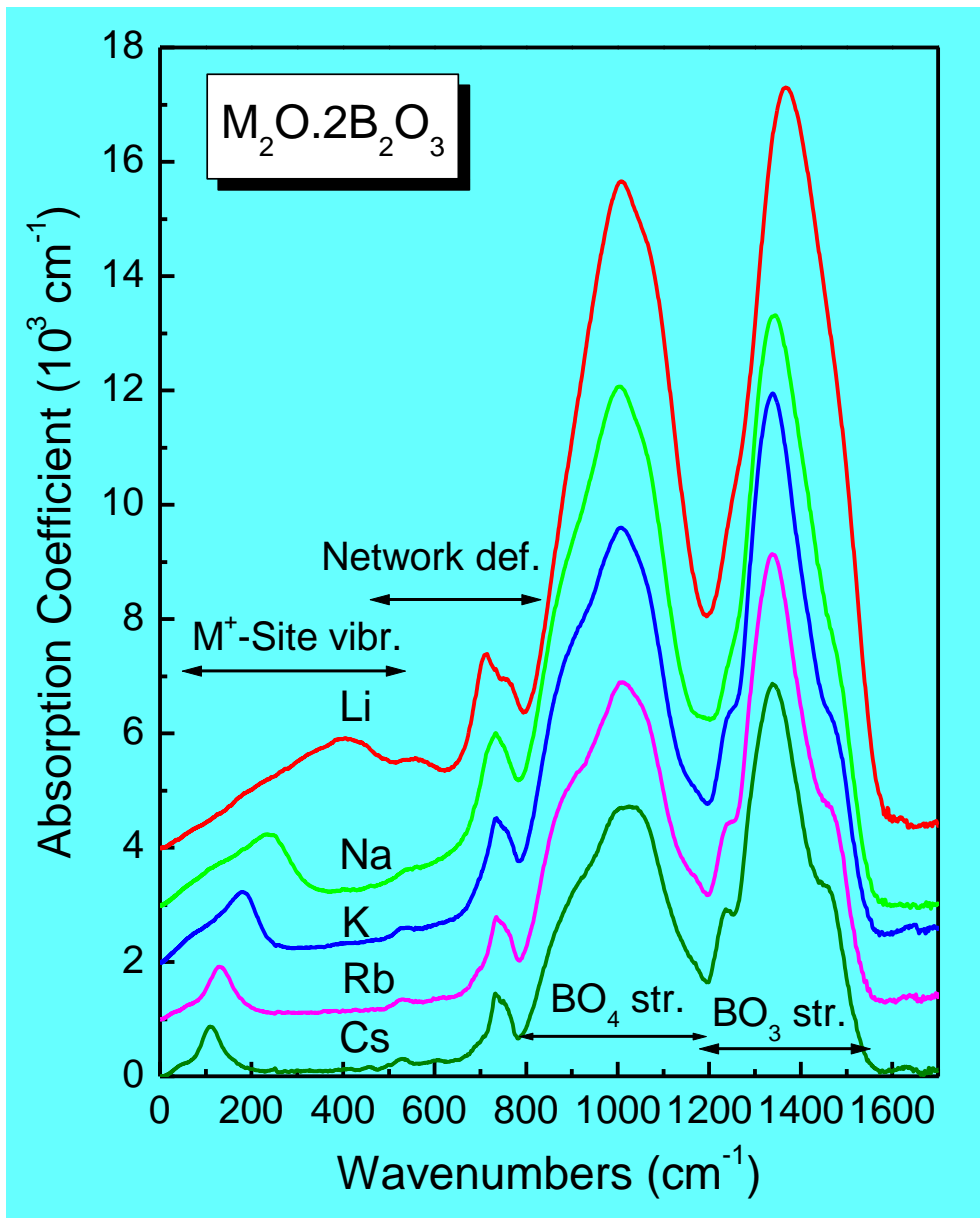
FGS2: FGS0 thermally exchanged in KNO_3 at 475 °C for 16h

FGS2A: FGS2 annealed in air at 475 °C for 16 h

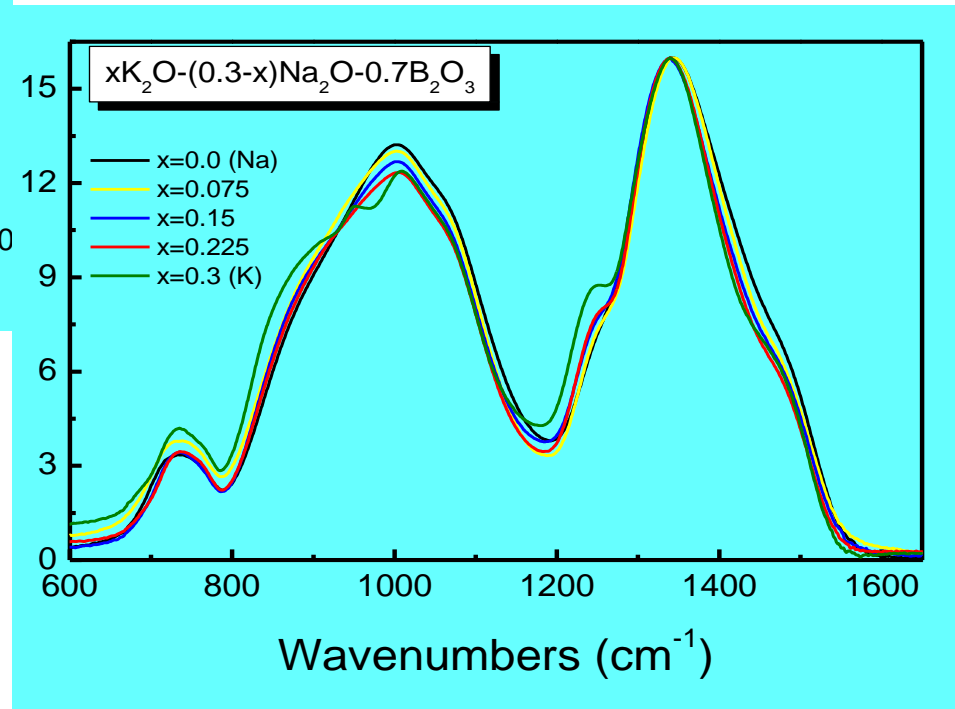
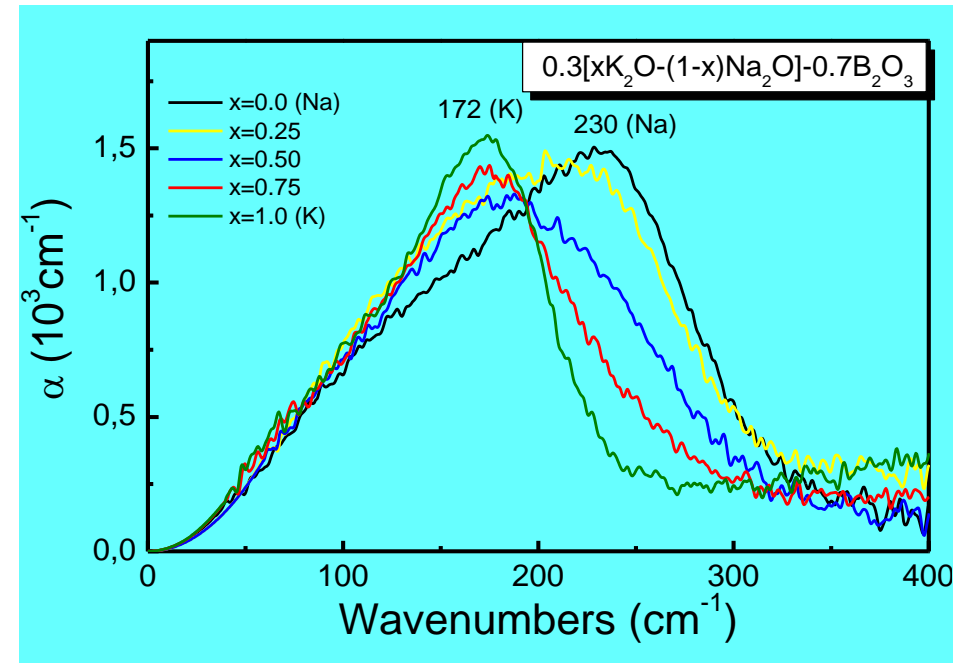
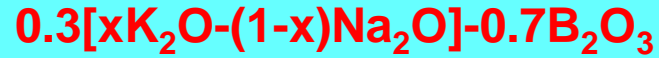


glass structure becomes less homogeneous

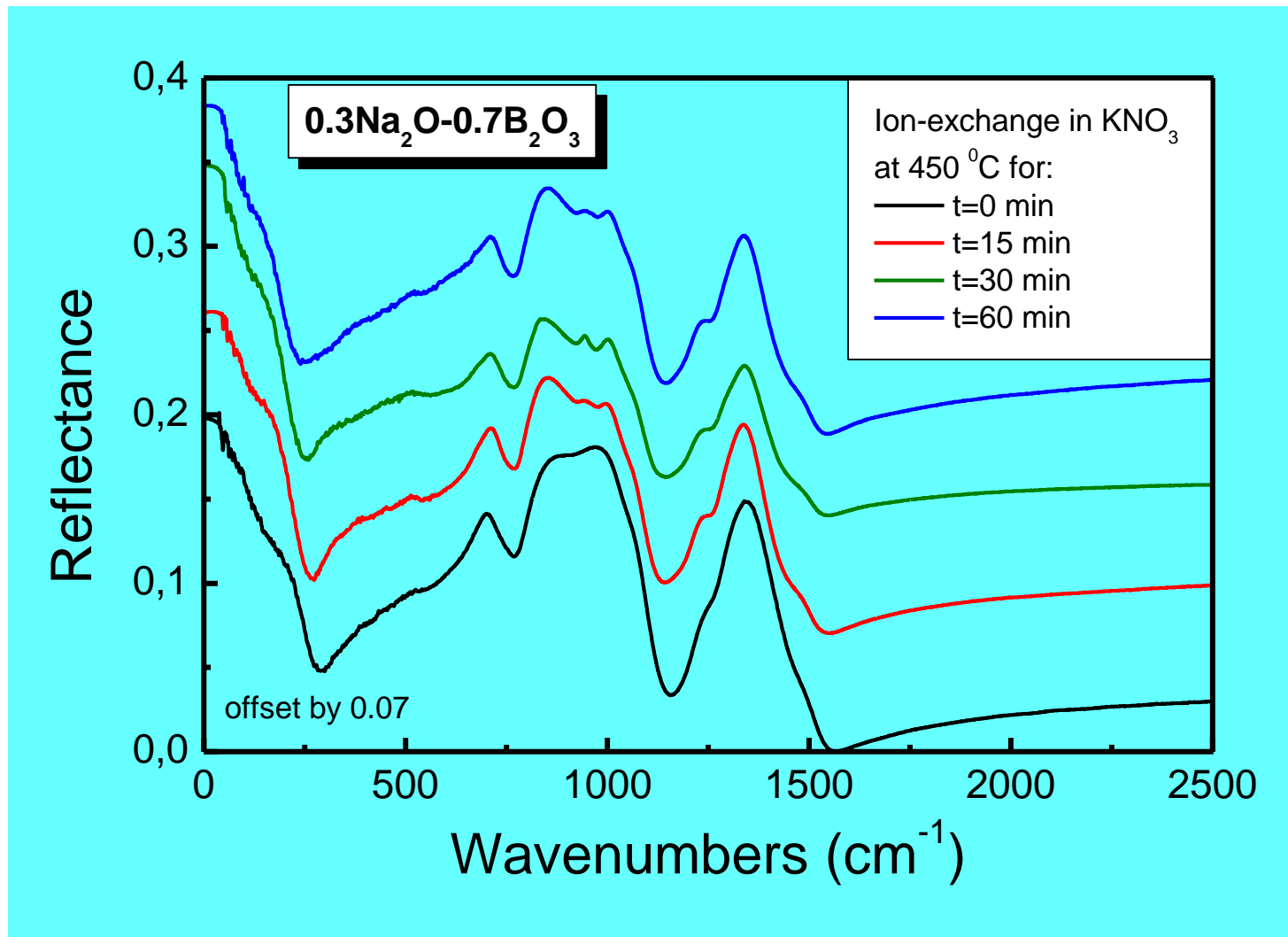
Infrared spectra of single alkali borate glasses



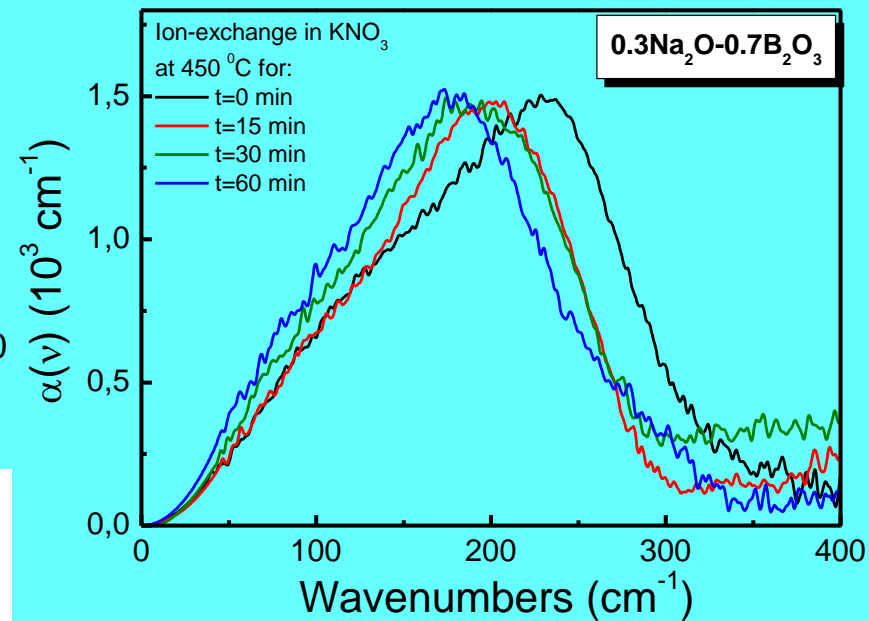
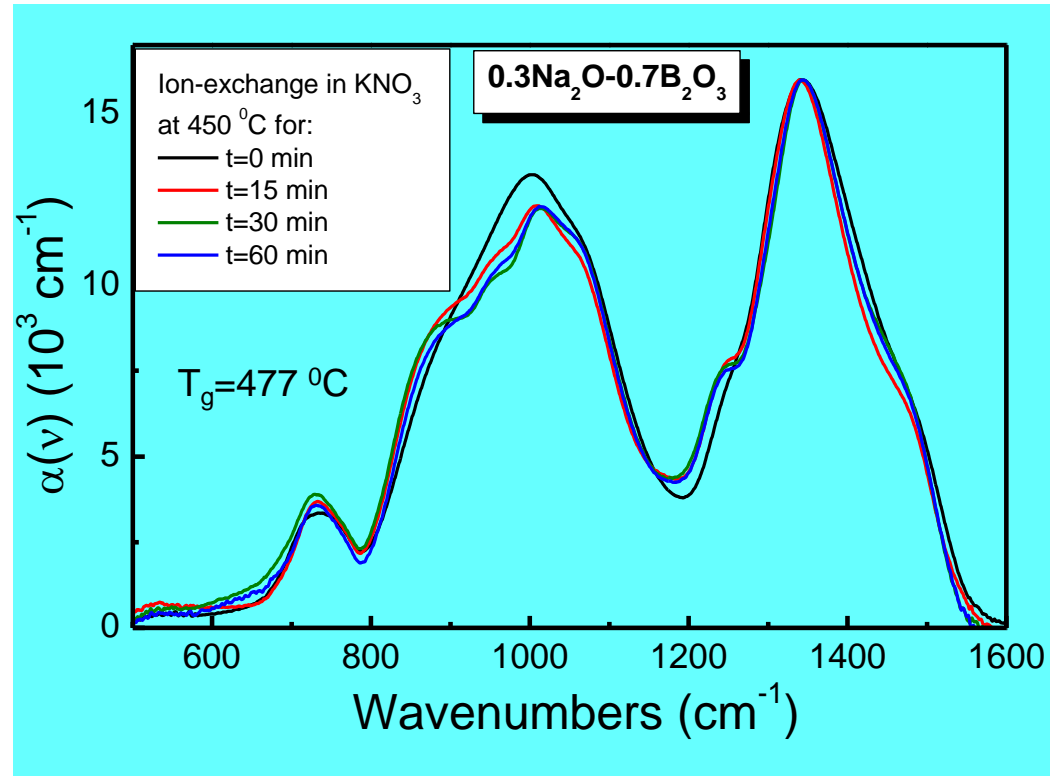
IR SPECTRA OF "SYNTHETIC" MIXED-CATION BORATE GLASSES

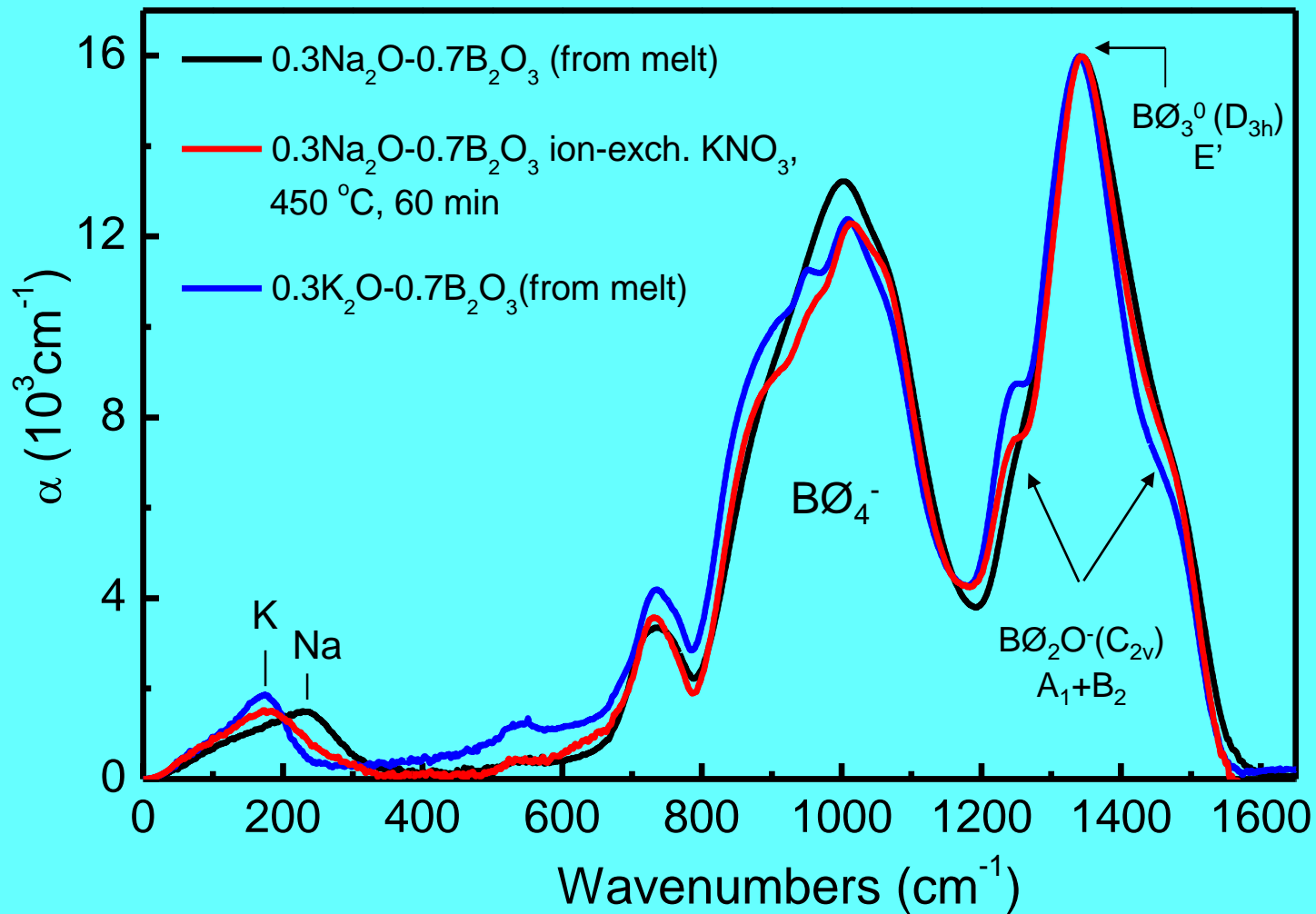


THERMALLY ION-EXCHANGED $0.3\text{Na}_2\text{O}-0.7\text{B}_2\text{O}_3$ GLASS: K^+/Na^+
IR reflectance spectra



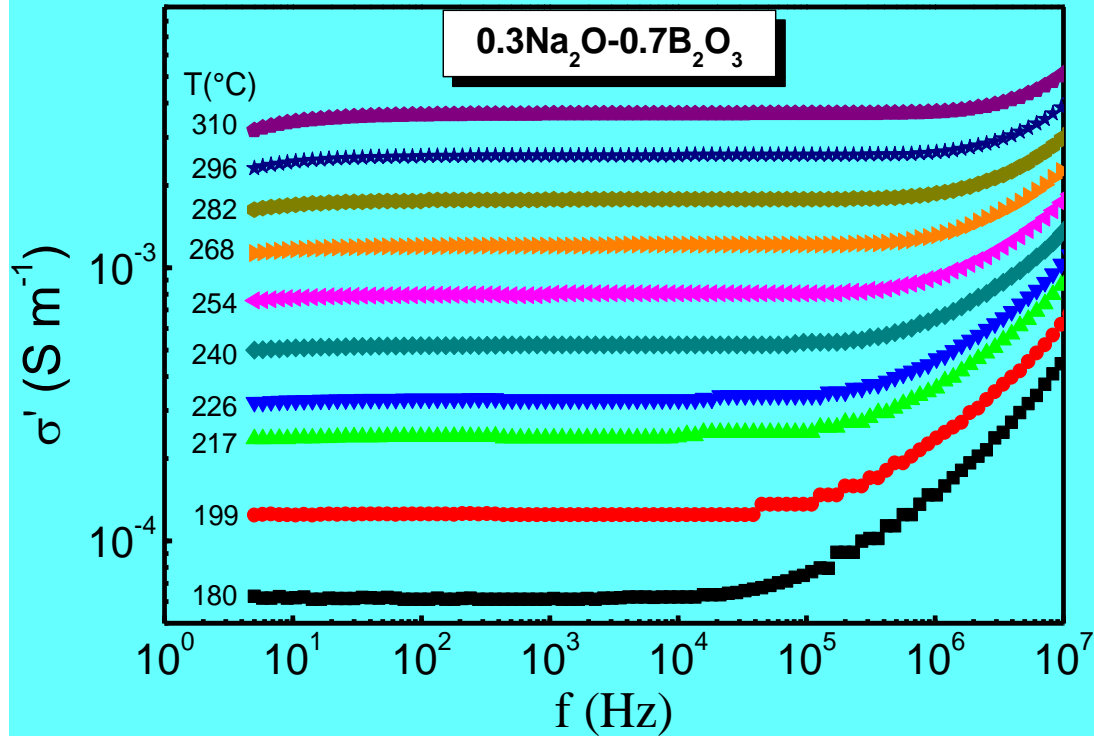
THERMALLY ION-EXCHANGED $0.3\text{Na}_2\text{O}-0.7\text{B}_2\text{O}_3$ GLASS: K^+/Na^+ IR absorption spectra



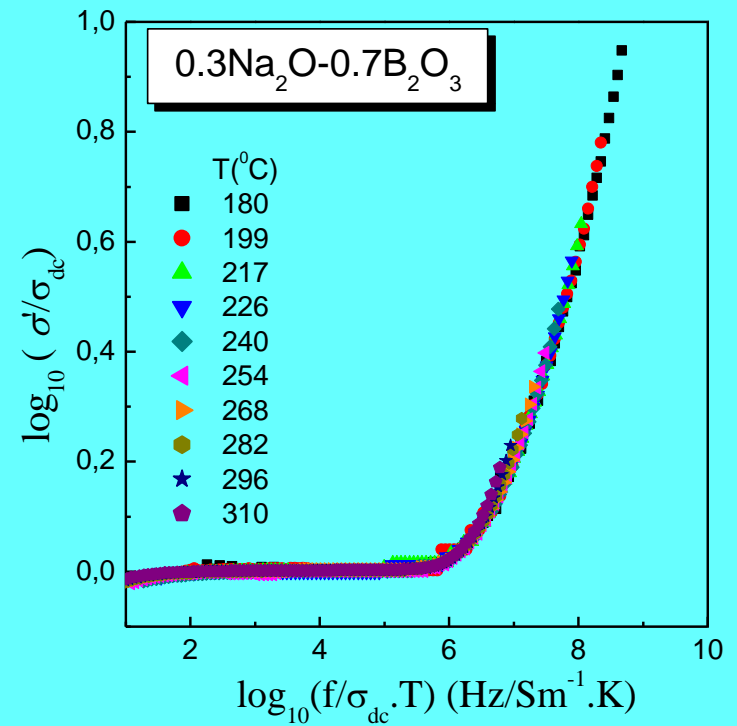


**local structure rearranges
to meet the needs of K^+ ions**

Conductivity spectra of the base glass: $0.3\text{Na}_2\text{O}-0.7\text{B}_2\text{O}_3$

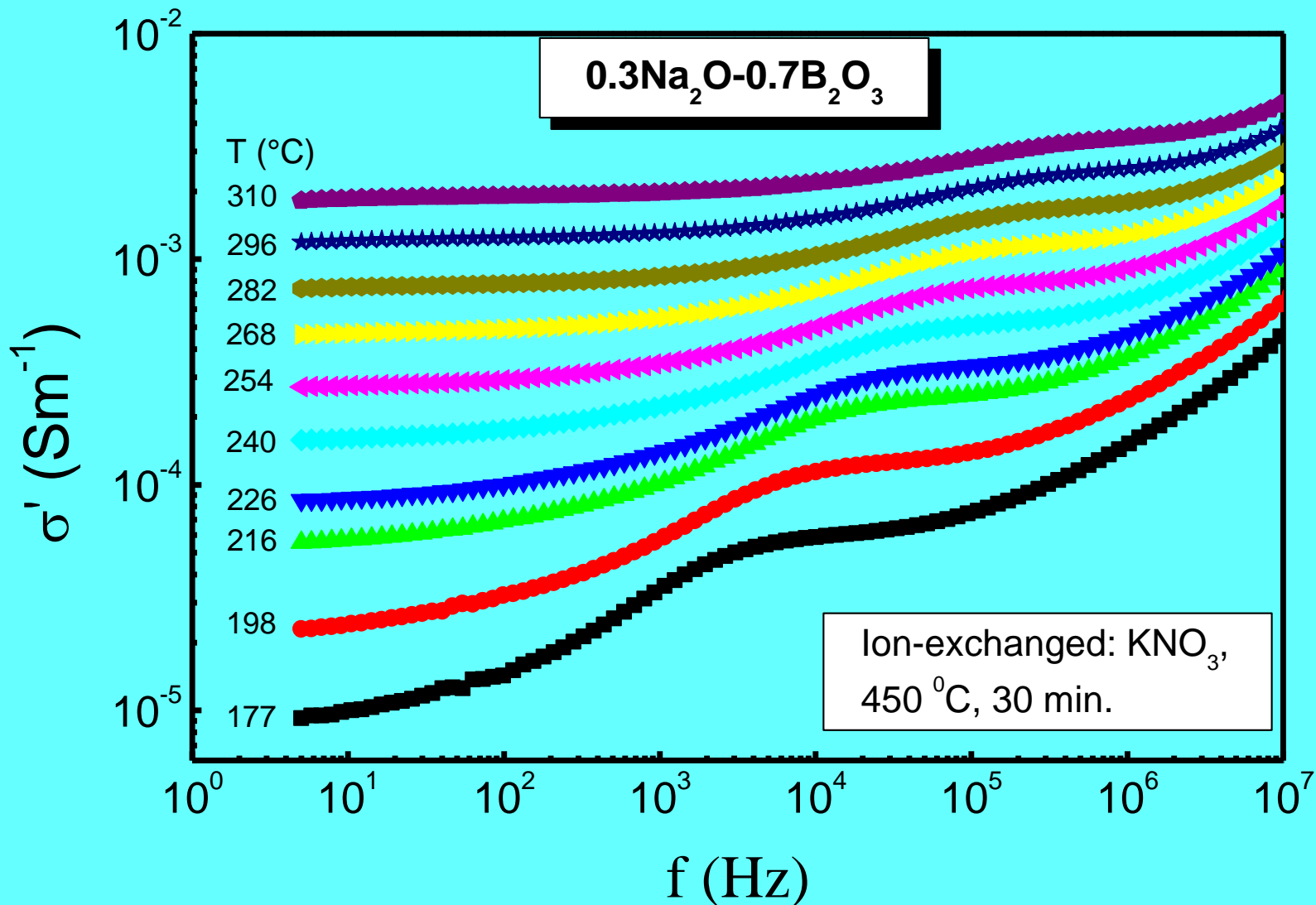


scaled conductivity spectra

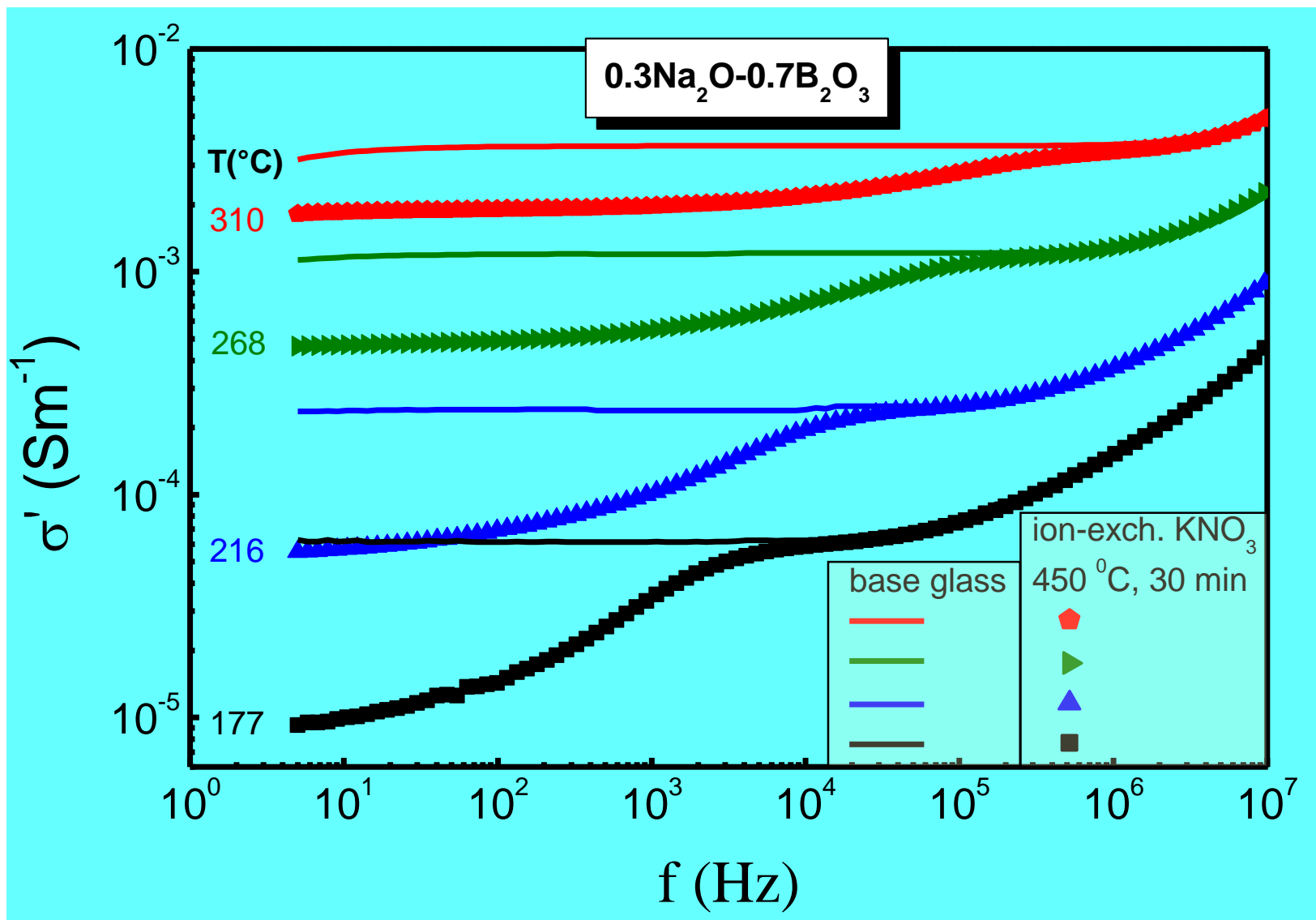


see: B. Roling, A.Happe, K. Funke & M.D. Ingram, Phys. Rev. Lett. 78 (1997) 2160.

Conductivity spectra of the $0.3\text{Na}_2\text{O}-0.7\text{B}_2\text{O}_3$ glass ion-exchanged in KNO_3

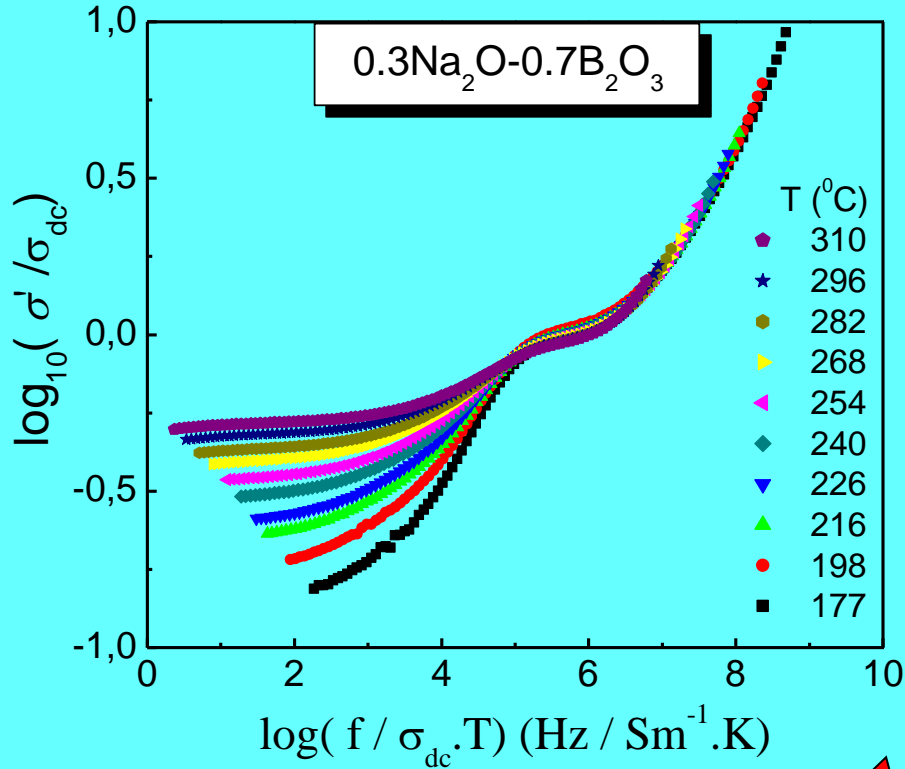


Comparison of conductivity spectra of the base glass $0.3\text{Na}_2\text{O}-0.7\text{B}_2\text{O}_3$ with those obtained after ion-exchange in KNO_3 at $450\text{ }^\circ\text{C}$ for 30 min

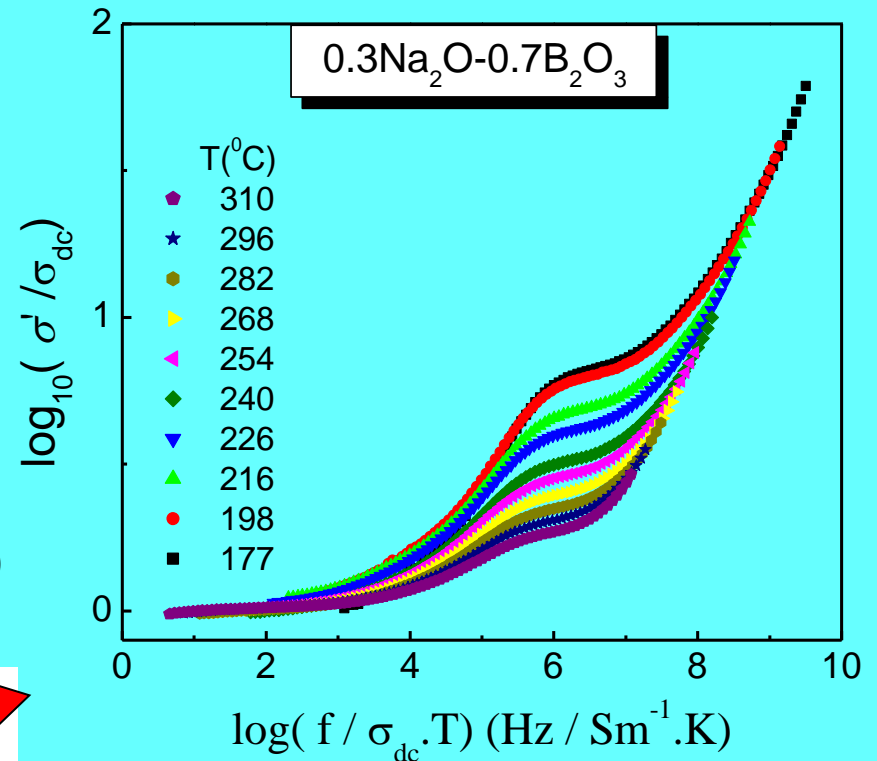


Scaled conductivity spectra of the $0.3\text{Na}_2\text{O}-0.7\text{B}_2\text{O}_3$ glass ion-exchanged in KNO_3 at 450°C for 30 min

scaled with σ_{dc} of the base glass

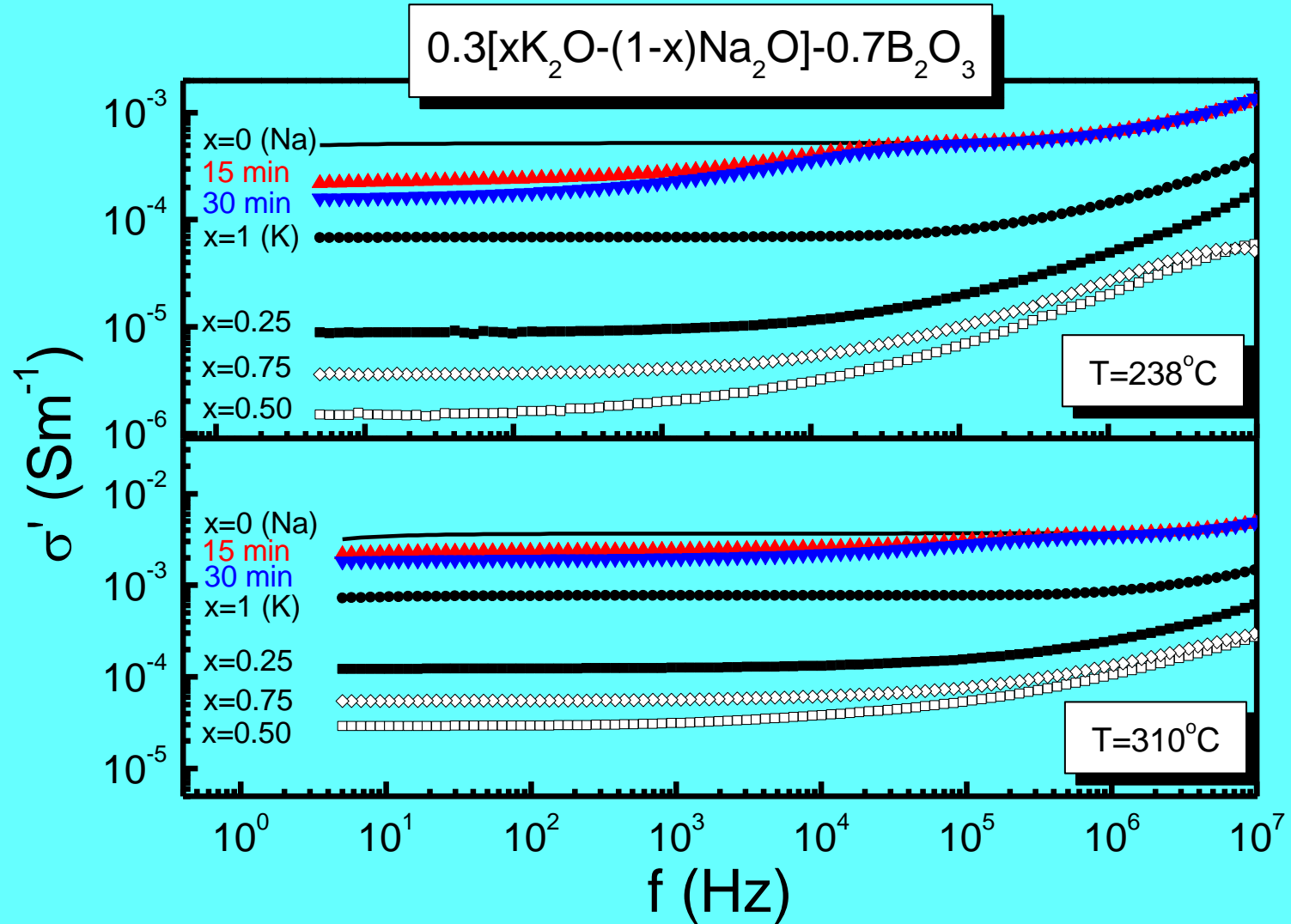


scaled with low-frequency σ_{dc} of the ion-exchanged glass



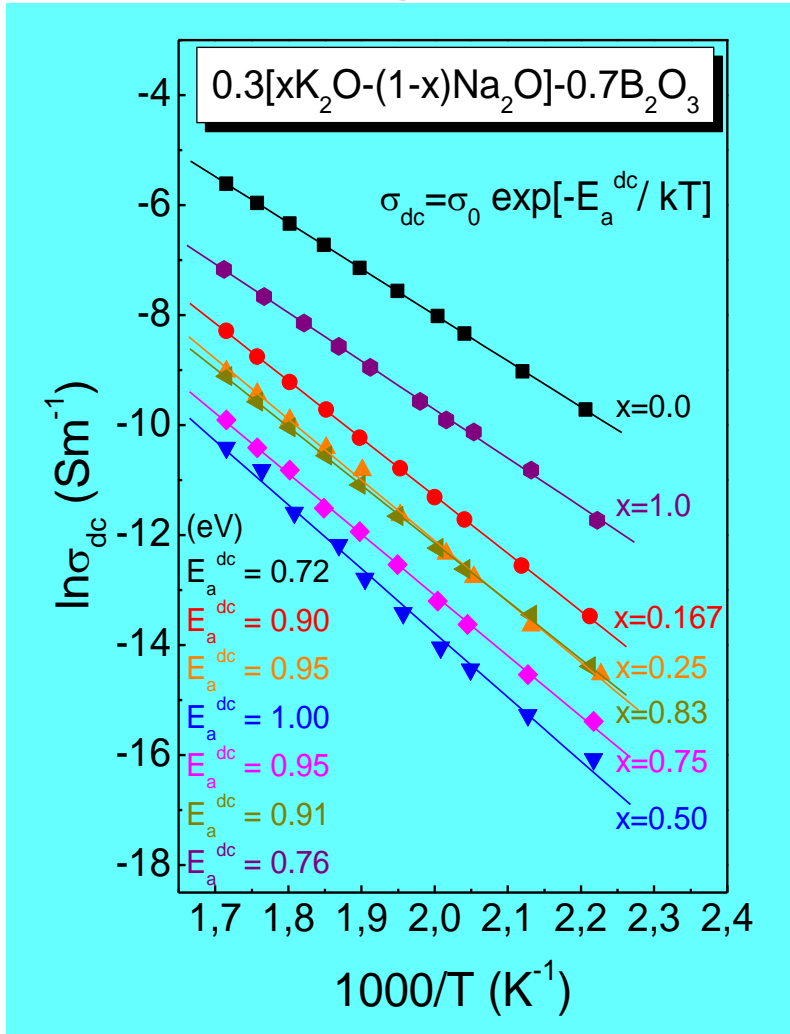
K⁺/Na⁺ ion exchange below T_g leads to the development of a highly resistive surface layer

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

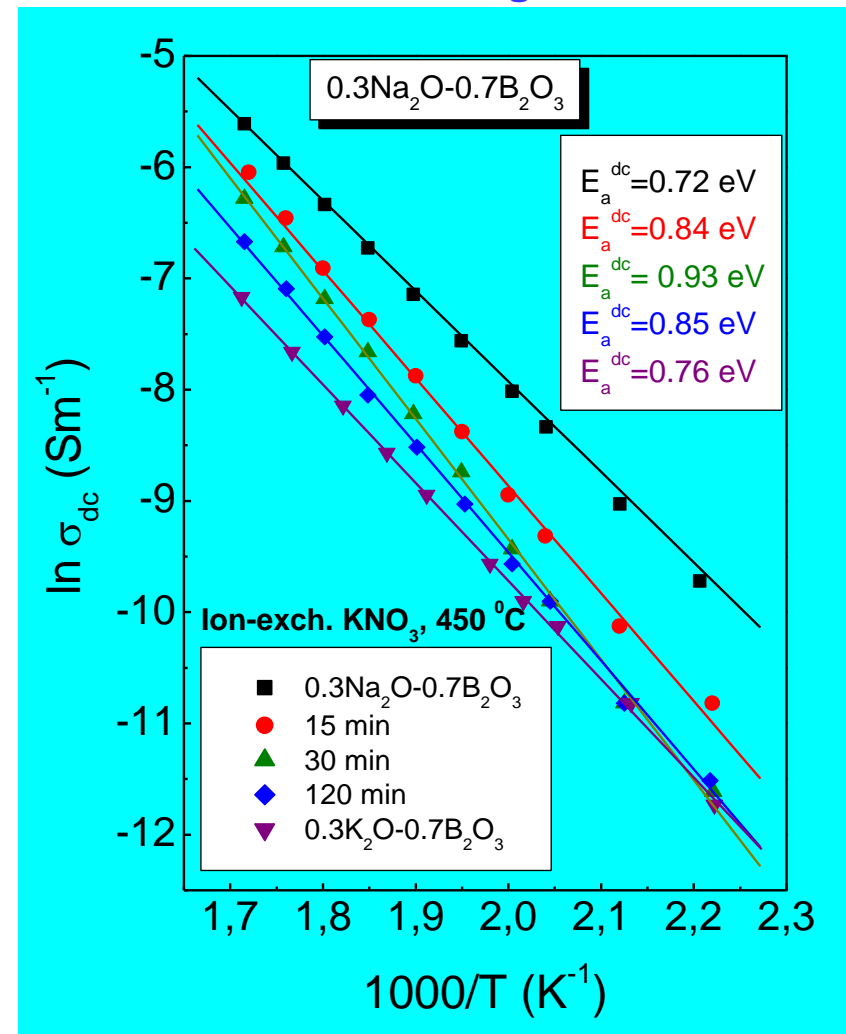


Comparison of activation energies for dc conductivity: melt-grown $0.3[xK_2O-(1-x)Na_2O]-0.7B_2O_3$ glasses vs ion-exchanged glasses

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

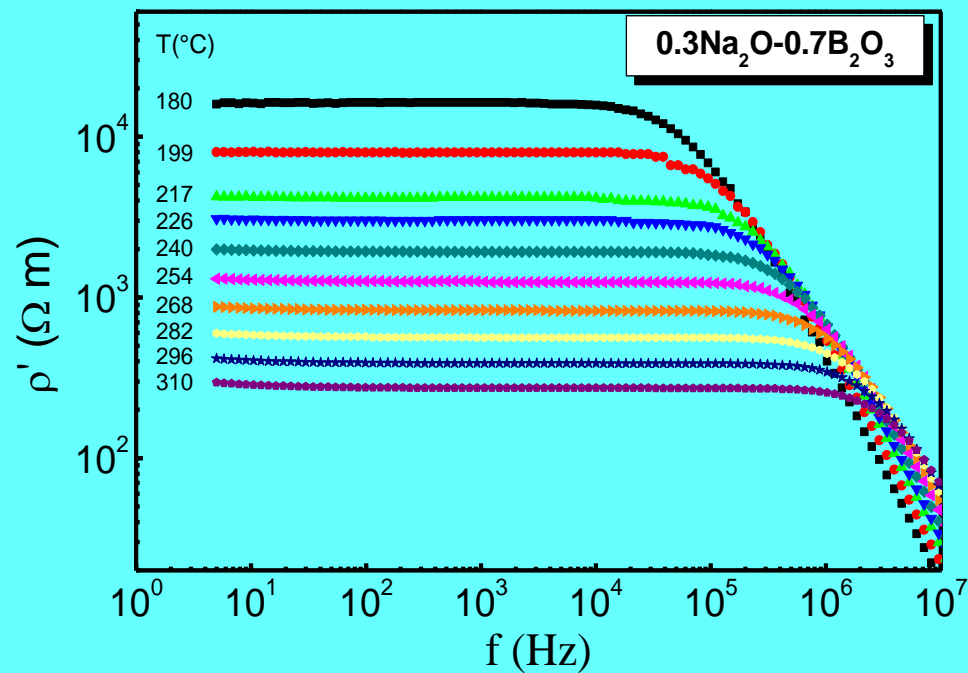
Complex conductivity:

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

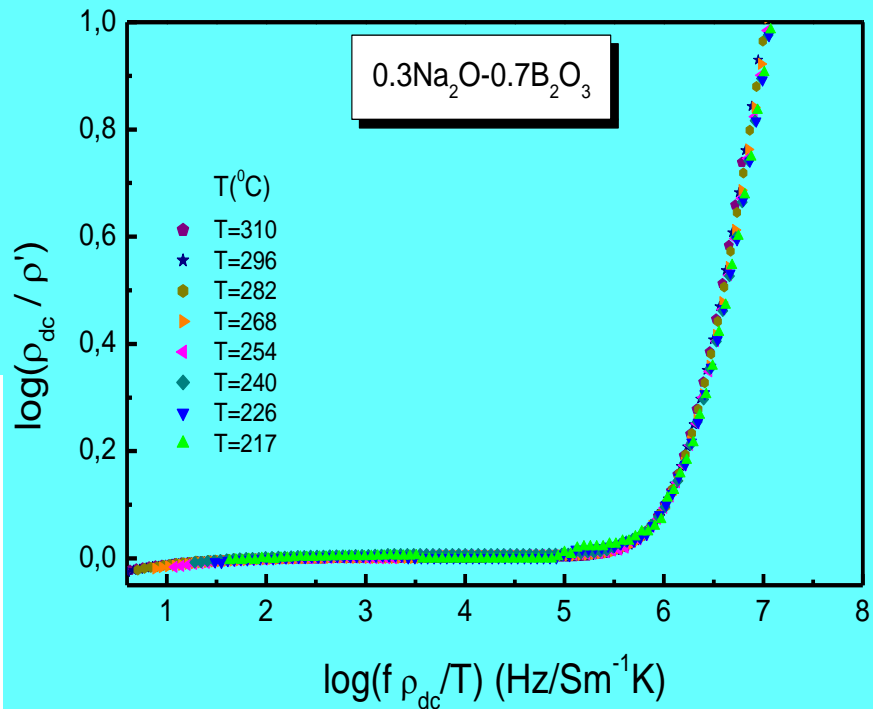
$$\sigma'(\omega) = \frac{\rho'(\omega)}{[\rho'(\omega)]^2 + [\rho''(\omega)]^2}$$

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

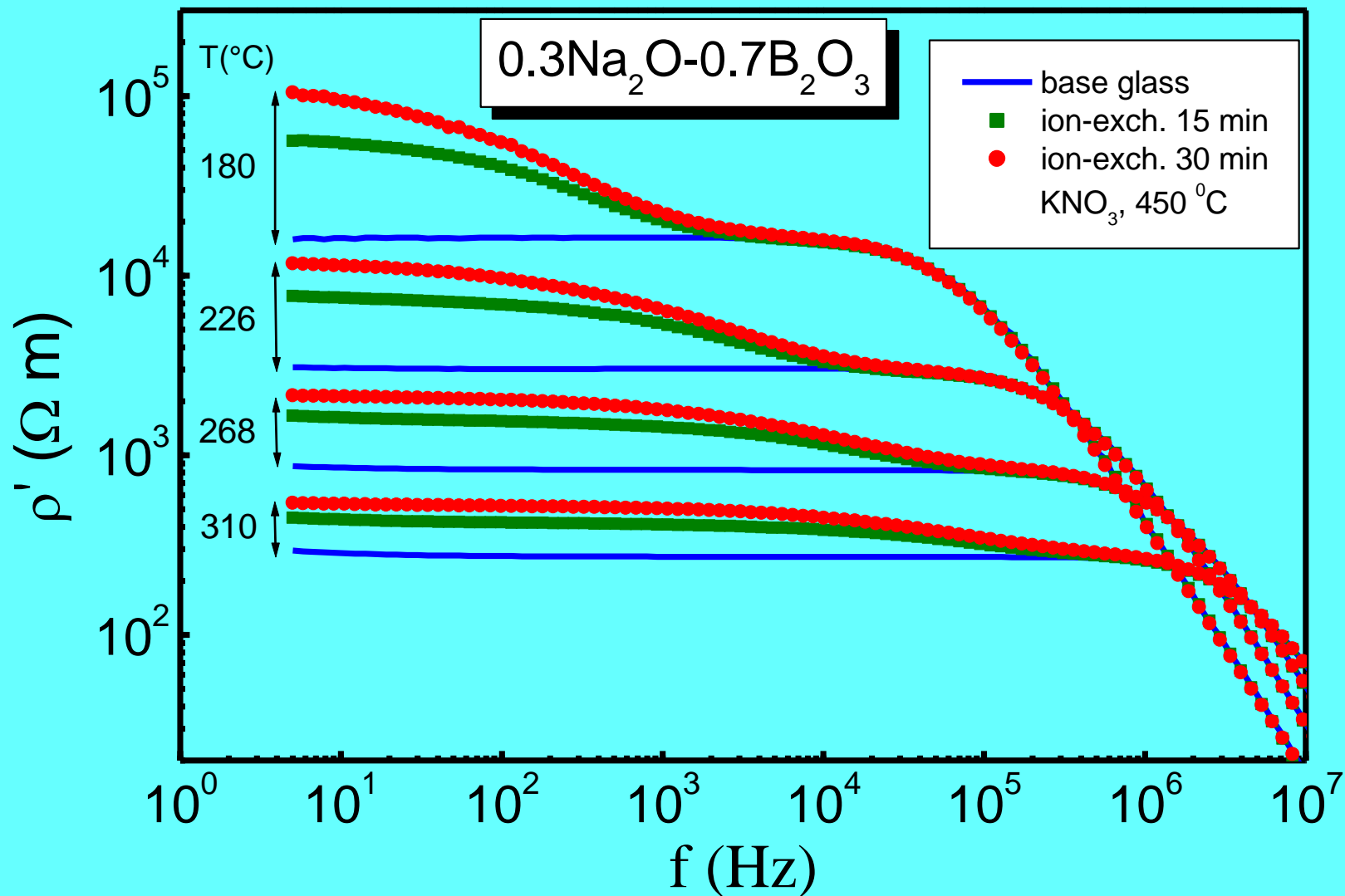
Resistivity spectra of the base glass: $0.3\text{Na}_2\text{O}-0.7\text{B}_2\text{O}_3$



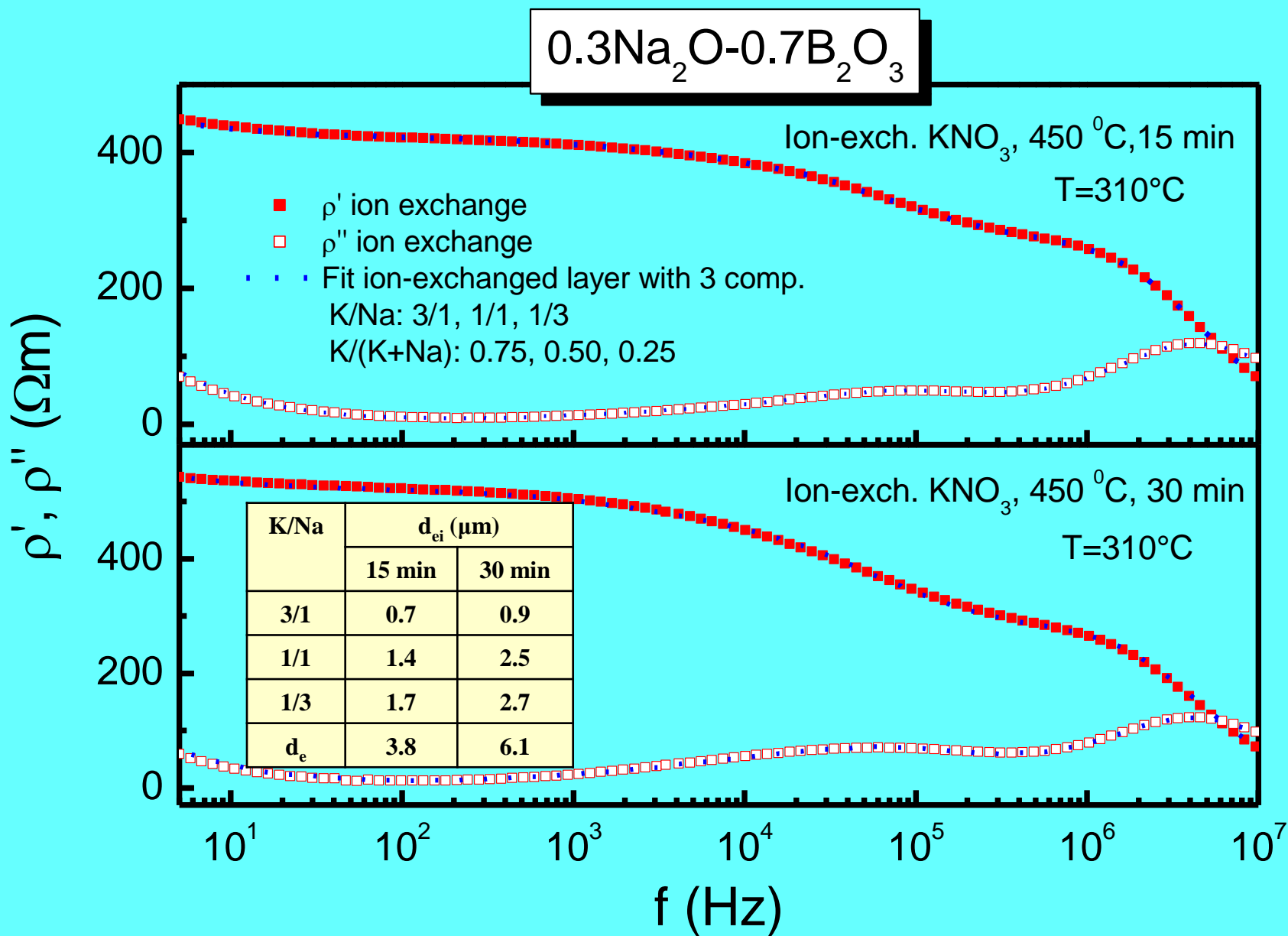
scaled resistivity spectra



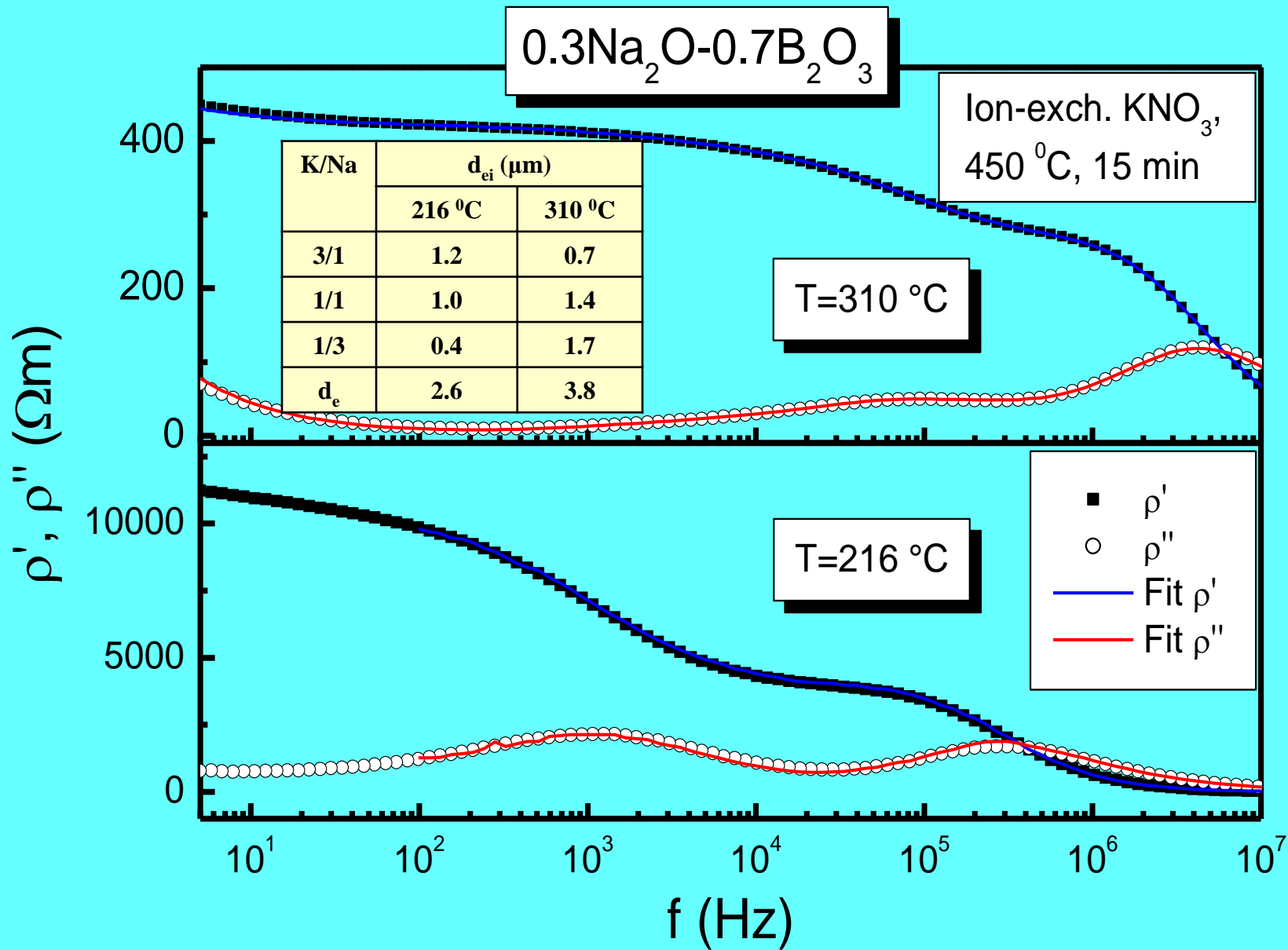
Resistivity spectra of the $0.3\text{Na}_2\text{O}-0.7\text{B}_2\text{O}_3$ glass ion-exchanged in KNO_3



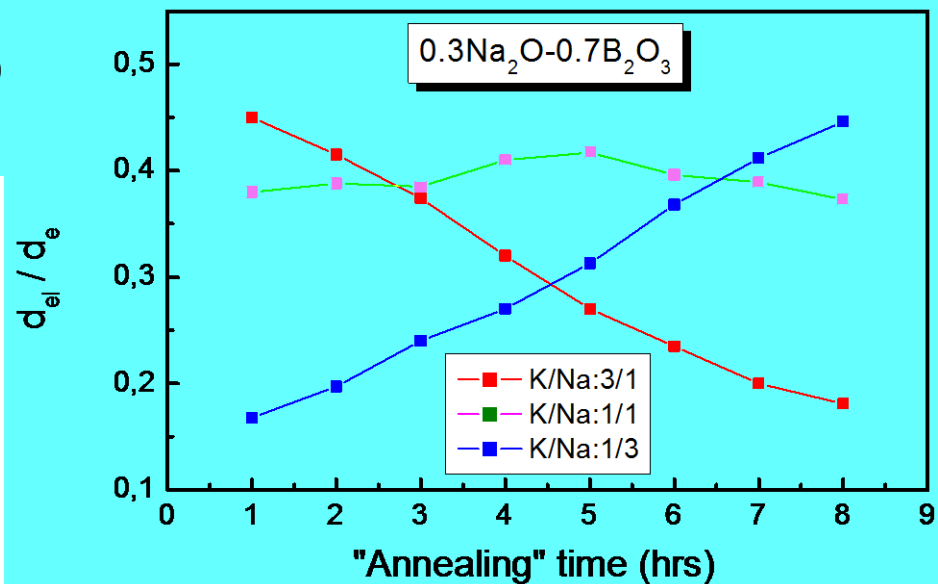
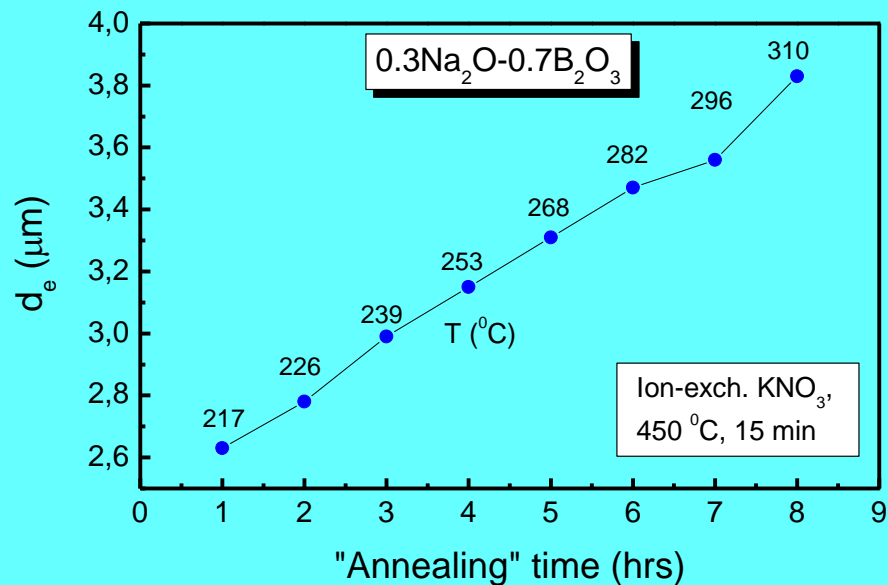
Resistivity spectra of the $0.3\text{Na}_2\text{O}-0.7\text{B}_2\text{O}_3$ glass ion-exchanged in KNO_3



“Annealing” of the 0.3Na₂O-0.7B₂O₃ ion-exchanged glass



"Annealing" of the $0.3\text{Na}_2\text{O}-0.7\text{B}_2\text{O}_3$ 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 (**C**ation **I**nduced **R**elaxations **O**f the **N**etwork, **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:



Sodium-borate glass:



⇒ 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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