# Special Topics in Relaxation in Glass and Polymers

# Lecture 6: Viscoelasticity II
# Bulk Viscoelasticity

**Dr. Ulrich Fotheringham**

***Research and Technology Development***

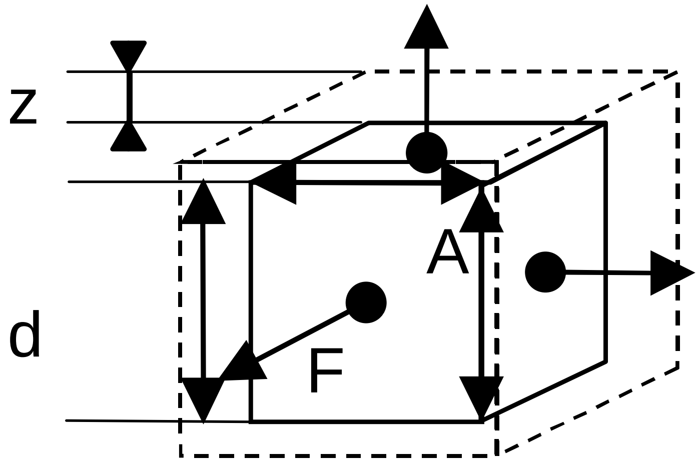
**SCHOTT AG**

SCHOTT
glass made of ideas

# Shear Viscoelasticity and Bulk Viscoelasticity

**As it has been said in the previous lecture, one has to distinguish between shear on one side and dilatation/compression (bulk viscoelasticity) on the other.**

## Bulk




$$F_x = D \cdot x \rightarrow \sigma_x = K \cdot 3 \cdot \varepsilon_x$$

$$F_y = \eta \cdot \frac{a}{d} \cdot \frac{dy}{dt} \rightarrow \sigma_y = \eta_V \cdot \frac{d\varepsilon_y}{dt}$$

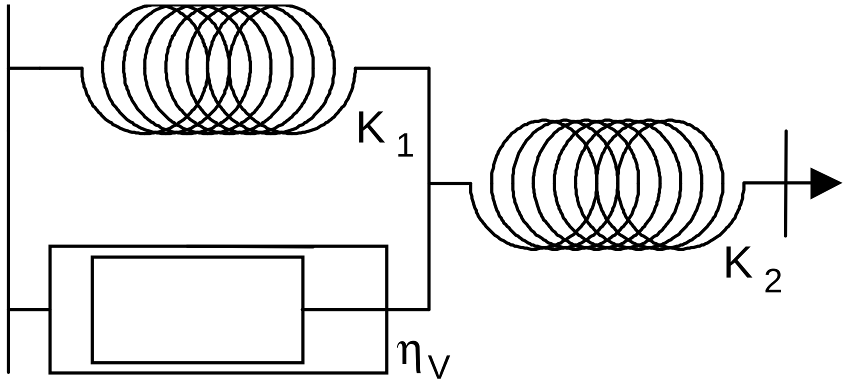
**The factor „3“ enters to allow for the fact that the bulk modulus does not relate the stress to the strain in one dimension but to the one in three dimensions, i.e. the volume change.**

**For the simple Kelvin-Voigt-model one gets assuming constant stress:**

$$\varepsilon = \frac{\sigma_0}{3K} \cdot \left(1 - e^{-t \cdot (3K/\eta_V)}\right) = \left(\frac{1}{3K} \cdot \left(1 - e^{-t \cdot (3K/\eta_V)}\right)\right) \cdot \sigma_0 =: J(t) \cdot \sigma_0$$

# 1st Realistic Picture of Bulk Relaxation: Kelvin-Voigt + Spring

**The simple Kelvin-Voigt-model, however, does not contain all features to be observed during the volume change of an inorganic glass being under pressure. It contains the delayed strain occurring at high temperatures, but not the instantaneous effect which is observable at all temperatures. The simplest suited model is the series of a Kelvin-Voigt-model and a spring. (Compared to the Burger-model, the second dashpot is missing which takes into account that in contrast to shear, creep is not possible.)**




**Compare the damper in a car!**

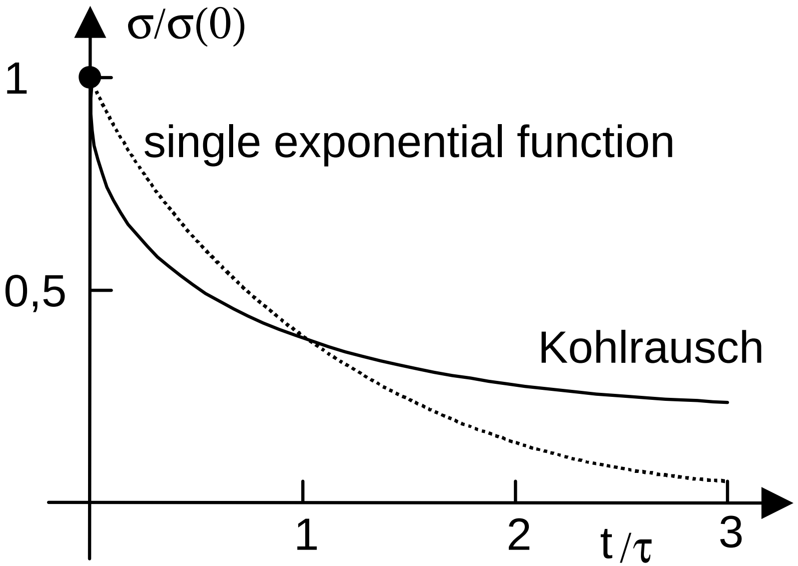
**For constant stress, one gets:**

$$\varepsilon = \left[\left(\frac{1}{3K_2}\right)+\left(\frac{1}{3K_1}\cdot\left(1-e^{-t\cdot(3K_1/\eta_V)}\right)\right)\right]\cdot\sigma_0 =: J(t)\cdot\sigma_0$$

**For constant strain, one gets:**

$$\sigma(t) = \frac{3\cdot K_1\cdot K_2}{K_1+K_2}\cdot\varepsilon_0+\frac{3\cdot K_2\cdot K_2}{K_1+K_2}\cdot\varepsilon_0\cdot e^{-t\cdot 3\cdot(K_1+K_2)/\eta_V)}$$

# Kohlrausch-Kinetics for Bulk Relaxation




**Again, an even better coincidence of theoretical and experimental data than with the Burger model is obtained, if the single exponential function from above is replaced with a stretched exponential or Kohlrausch(-Williams-Watts)-function.**

**For constant stress one gets:**

$$\varepsilon = \left[ \frac{1}{3K_0} + \frac{1}{3}\left( \frac{1}{K_\infty} - \frac{1}{K_0} \right) \cdot \left( 1 - e^{-(t/\tau_d)^{b_d}} \right) \right] \cdot \sigma_0 =: J(t) \cdot \sigma_0$$

**$J(t)$ is the time-dependent compliance; $\tau_d$ and $b_d$ are retardation parameters.**

**For constant strain one gets**

$$\sigma(t) = \left[ 3 \cdot K_\infty + (3 \cdot K_0 - 3 \cdot K_\infty) \cdot e^{-(t/\tau_x)^{b_x}} \right] \cdot \varepsilon_0 =: K(t) \cdot \varepsilon_0$$

**$K(t)$ is the time-dependent bulk modulus; $\tau_x$ and $b_x$ are relaxation parameters.**

# Boltzmann´s superposition principle

**In general it is assumed that the stress effects arising from strain contributions imposed at different times overlay without interfering and vice versa:**

$$\sigma(t) = \sum \Delta\varepsilon_{(at\ the\ time\ t')} \cdot \left[ 3 \cdot K_\infty + (3 \cdot K_0 - 3 \cdot K_\infty) \cdot e^{-((t-t')/\tau_x)^{b_x}} \right]$$

$$\approx 3 \cdot K_\infty \cdot \varepsilon(t) + (3 \cdot K_0 - 3 \cdot K_\infty) \cdot \int_0^t e^{-((t-t')/\tau_x)^{b_x}} \cdot \frac{d\varepsilon(t')}{dt'} \cdot dt'$$

**One may write introducing relaxation function Ψ**

$$\sigma(t) = 3 \cdot K_\infty \cdot \varepsilon(t) + (3 \cdot K_0 - 3 \cdot K_\infty) \cdot \int_0^t \Psi\left(\frac{t-t'}{\tau_x}\right) \cdot \frac{d\varepsilon(t')}{dt'} \cdot dt'$$

**and retardation function Φ**

$$\varepsilon(t) = \frac{1}{3K_\infty} \cdot \sigma(t) - \frac{1}{3}\left(\frac{1}{K_\infty} - \frac{1}{K_0}\right) \cdot \int_0^t \Phi\left(\frac{t-t'}{\tau_d}\right) \cdot \frac{d\sigma(t')}{dt'} \cdot dt'$$

# Relaxation Retardation

**Laplace-Transform yields:**

$$L(\sigma) = 3 \cdot K_\infty \cdot L(\varepsilon) + (3 \cdot K_0 - 3 \cdot K_\infty) \cdot L(\Psi) \cdot s \cdot L(\varepsilon)$$

**and**

$$L(\varepsilon) = \frac{1}{3K_\infty} \cdot L(\sigma) - \frac{1}{3}\left(\frac{1}{K_\infty} - \frac{1}{K_0}\right) L(\Phi) \cdot s \cdot L(\sigma)$$

**This allows the mutual conversion of relaxation and retardation parameters.**

# Prony Series

**For computational purposes, the Kohlrausch-function may again be represented by a number of single exponentials (Prony-series):**

$$e^{-(t/\tau)^b} = \sum_i v_i \cdot e^{-t/\tau_i} \quad , \quad \sum_i v_i = 1$$

# Temperature dependence of the relaxation and retardation times

**Again, an Arrhenius ansatz is made:** $\tau = \tau_0 \cdot e^{\frac{H}{R \cdot T}}$

## Some exercises:

1. **Consider the combination of a Kelvin-Voigt model and a spring as 1st realistic representation of bulk viscoelasticity. Consider constant strain. What is $\sigma(0)$?**

2. **Consider the relaxation function in case of single-step strain, $\varepsilon(t) = \varepsilon_0 \cdot \Theta(t)$, $\Theta$: Heaviside function. Calculate $\sigma(t)$ from the below formula (with the script of Prof. Cox, it is very simple!)**

$$\sigma(t) = 3 \cdot K_\infty \cdot \varepsilon(t) + (3 \cdot K_0 - 3 \cdot K_\infty) \cdot \int_0^t \Psi\left(\frac{t-t'}{\tau_x}\right) \cdot \frac{d\varepsilon(t')}{dt'} \cdot dt'$$

3. **Consider the Arrhenius law. With H = 8380 J/mole and the gas constant R = 8.38 J/(mole K), which temperature step is necessary to double relaxation time $\tau$ (start temperature: 600°C)?**

# Bulk relaxation experiments by University of Erlangen-Nürnberg, Clemson-University, Bayrisches Geoinstitut, and SCHOTT AG I

## Measurement of the Dimensional Relaxation Effect in Optical Glasses

diploma thesis

| | |
|---|---|
| Submitted by: | Christian Bienert |
| Major: | materials science |
| Referent: | Prof. Dr. Rudolf Weißmann |
| Advisors: | Dr. Ulrich Fotheringham |
| | Prof. Kathleen Richardson |
| Time frame: | from October, 3rd 2005 |
| | to July, 3rd 2006 (9 months) |

Friedrich-Alexander University Erlangen-Nuremberg
Department of Materials Science III Glass and Ceramics
Martensstr. 5, 91058 Erlangen, ww3@ww.uni-erlangen.de

DGG, FA I Würzburg, 17.03.2009

## Optische und volumetrische Messungen an Gigapascal-verdichteten optischen Gläsern

U. Fotheringham[1], O. Sohr[1], P. Fischer[1], G. Westenberger[1], D. Frost[2], C. Bienert[3], R. Weißmann[3], K. Richardson[4]

[1]SCHOTT AG, Mainz, [2]Bayrisches Geoinstitut, Universität Bayreuth, [3]Universität Erlangen-Nürnberg, [4]Clemson University

SCHOTT glass made of ideas

# Bulk relaxation experiments by Erlangen-Nürnberg, Clemson, Bayrisches Geoinsitut, SCHOTT II

## Glasses



### Gläser II: Thermomechanische Eigenschaften, Zusammensetzung

| Sample | K 7 | N-BaF 10 | N-LaK 12 | N-LaSF 9 |
|---|---|---|---|---|
| ρ [g/cm$^3$] | 2.53 | 3.75 | 4.10 | 4.41 |
| $T_g$ [°C] | 513 | 660 | 614 | 683 |
| $T_{10x13.0}$ [°C] | 528 | 652 | 615 | 700 |
| Aluminum Oxide | | 1-10 | | |
| Antimony Trioxide | | < 1 | < 1 | < 1 |
| Arsenic Trioxide | < 1 | | | < 1 |
| Barium Oxide | | 40-50 | 40-50 | 20-30 |
| Boron Oxide | 1-10 | 1-10 | 10-20 | 1-10 |
| Lanthanum Oxide | | | 10-20 | 20-30 |
| Lead Oxide | < 1 | | | |
| Niobium Pentoxide | | | | 1-10 |
| Potassium Oxide | 10-20 | | | |
| Silica | 60-70 | 30-40 | 10-20 | 10-20 |
| Sodium Oxide | 1-10 | | | 1-10 |
| Titanium Oxide | < 1 | 1-10 | < 1 | 10-20 |
| Zinc Oxide | 1-10 | 1-10 | | 1-10 |
| Zirconium Oxide | | 1-10 | < 1 | 1-10 |

SCHOTT glass made of ideas

Measurement of the Dimensional Relaxation Effect in Optical Glasses

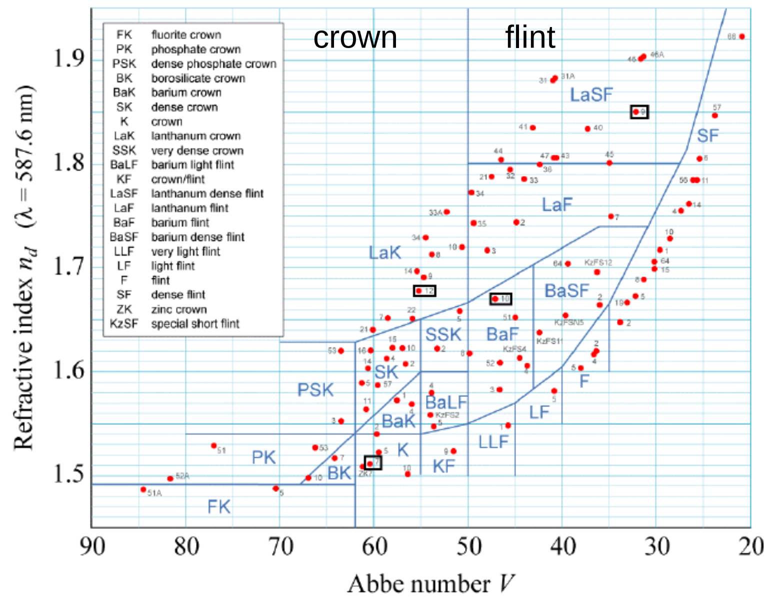
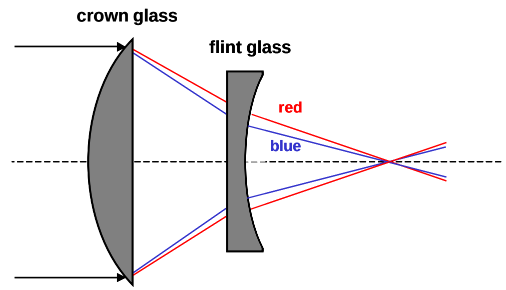



Figure 6: Abbe diagram of optical glasses[16].



# Bulk relaxation experiments by Erlangen-Nürnberg, Clemson, Bayrisches Geoinstitut, SCHOTT III

**Multi-Anvil-Device experiments:**

**Pressure in the Gigapascal range**

DGG, FA I    Würzburg, 17.03.2009

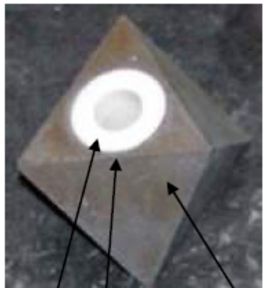
## Multi-Anvil-Device I: Aufbau

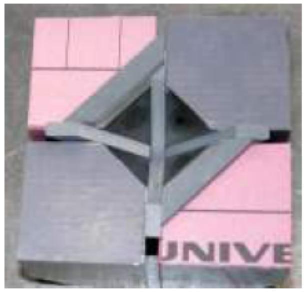
3,8mm

3,8mm

Samples are wrapped in Iridium foil

Einpacken in Ir-Folie






$ZrO_2$

MgO-Oktaeder mit Heizelement

WC-Kuben; eine Ecke abgesägt; durch dickes Papier getrennt

Position des Thermoelementes

Thermocouple

Heating element in the octa-eder

Tungsten carbide cubes with one corner cut off


Hydraulische Presse, z.B. Sumitomo 1200 (400 bar Öldruck entsprechen 5 GPa)

Hydraulic press

SCHOTT glass made of ideas

# Bulk relaxation experiments by Erlangen-Nürnberg, Clemson, Bayrisches Geoinstitut, SCHOTT IV

## Multi-Anvil-Device experiments:

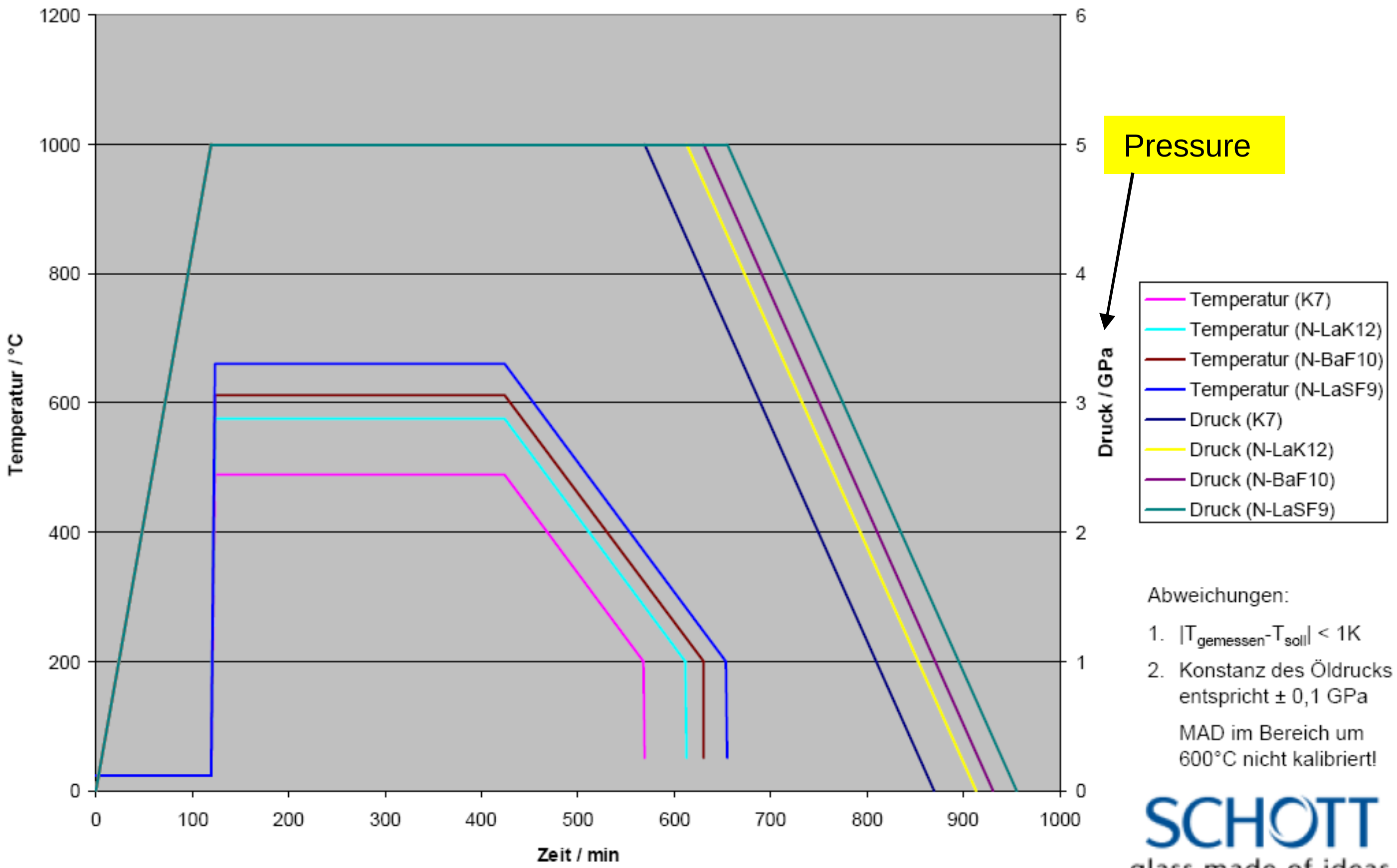
## Temperature and pressure loads

DGG, FA I — Würzburg, 17.03.2009

### Multi-Anvil-Device II: Lastkurven

| Sample | K 7 | N-BaF 10 | N-LaK 12 | N-LaSF 9 |
|---|---|---|---|---|
| Pressure [GPa] | 5 | 5 | 5 | 5 |
| $T_g$ [°C] | 513 | 660 | 614 | 683 |
| $T_{ext}$ [°C] | 488 | 612 | 575 | 660 |

Druck- und Temperaturlast im MAD (Sollwerte)




SCHOTT glass made of ideas

# Bulk relaxation experiments by Erlangen-Nürnberg, Clemson, Bayrisches Geoinstitut, SCHOTT V

**Multi-Anvil-Device experiments:**

**Density measurements:**

**when and how**



## Dichte I: Messungen

wann:

nach Probenpräparation (5×)

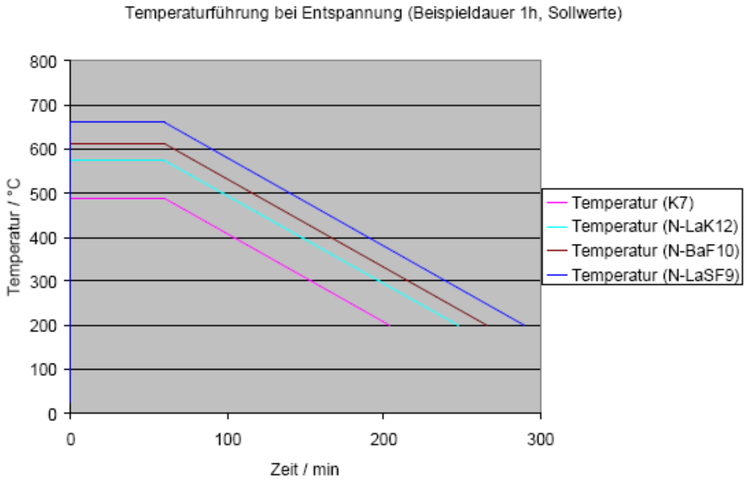
1st measurement after sample preparation

nach Verdichtung (5×)

2nd measurement after densification

3rd measurement after relaxation in forced convection furnace

nach Entspannungsintervall im Umluftofen (10×)




wie:

Messung nach Archimedes mit wäßriger Lösung von Nekal BX trocken (1g/l; BASF; 0.9977190 g/cm³ bei 25°; „Nekal“ kommt von „netzt kalt“ und ist ein Meilenstein der Tensidentwicklung)

Density measurement after Archimedes in Nekal solution (Nekal: tenside from BASF)

# Bulk relaxation experiments by Erlangen-Nürnberg, Clemson, Bayrisches Geoinstitut, SCHOTT VI

**Multi-Anvil-Device experiments:**

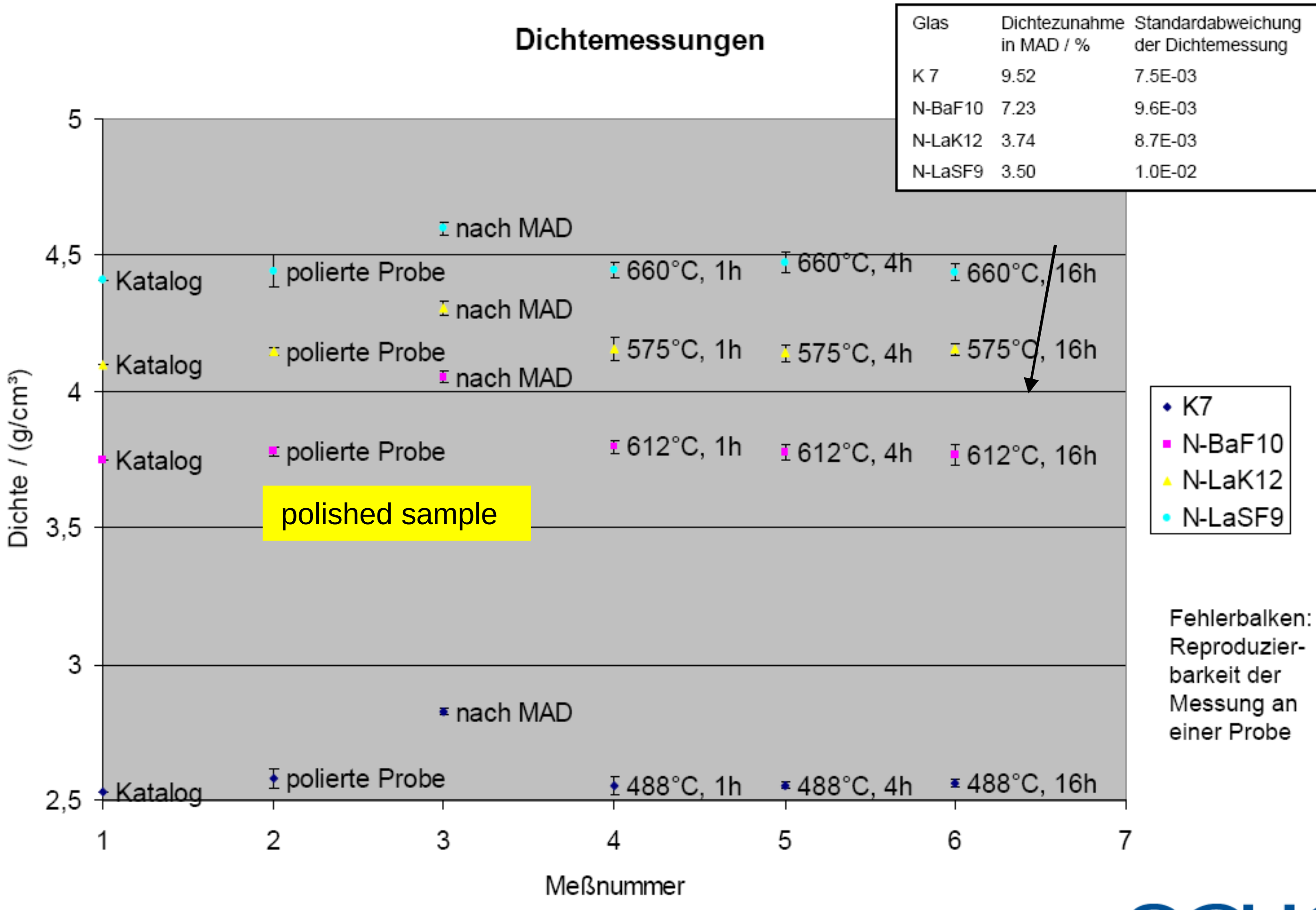
**Density measurements:**

**results**



## Dichte II: Meßergebnisse nach Verdichtung und Entspannung

| Glas | Dichtezunahme in MAD / % | Standardabweichung der Dichtemessung |
|---|---|---|
| K 7 | 9.52 | 7.5E-03 |
| N-BaF10 | 7.23 | 9.6E-03 |
| N-LaK12 | 3.74 | 8.7E-03 |
| N-LaSF9 | 3.50 | 1.0E-02 |

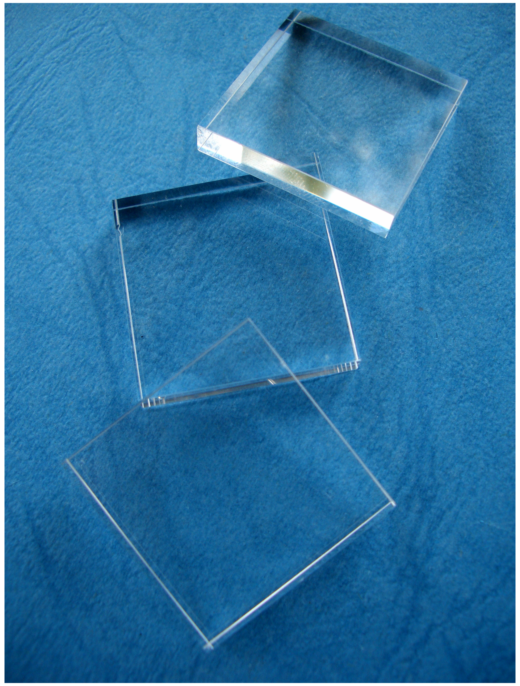



Fehlerbalken: Reproduzierbarkeit der Messung an einer Probe

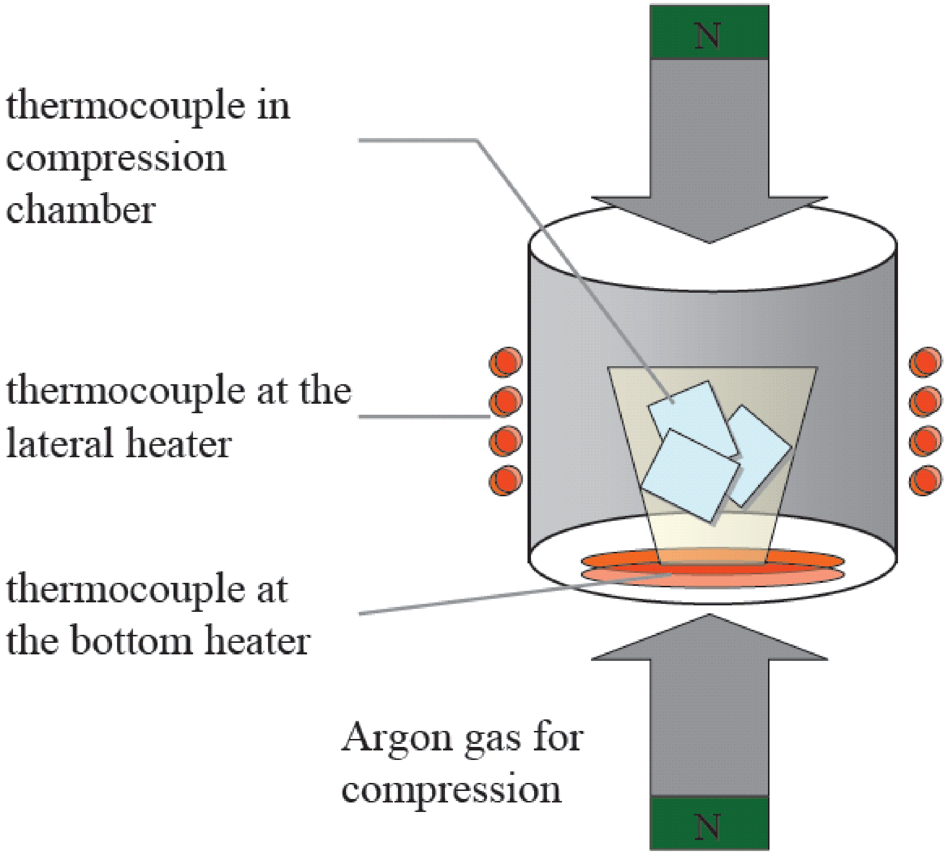
# Bulk relaxation experiments by Erlangen-Nürnberg, Clemson, Bayrisches Geoinstitut, SCHOTT VII

## Hot Isostatic Press experiments:

## Samples and device



polished sample




**Experimental conditions for the sample glasses in HIP**

| Sample | K 7 | N-BaF 10 | N-LaK 12 | N-LaSF 9 |
|---|---|---|---|---|
| **Pressure [MPa]** | **150** | **150** | **150** | **150** |
| $T_g$ [°C] | 513 | 660 | 614 | 683 |
| **$T_{ex}$[°C]** | **488** | **612** | **575** | **660** |

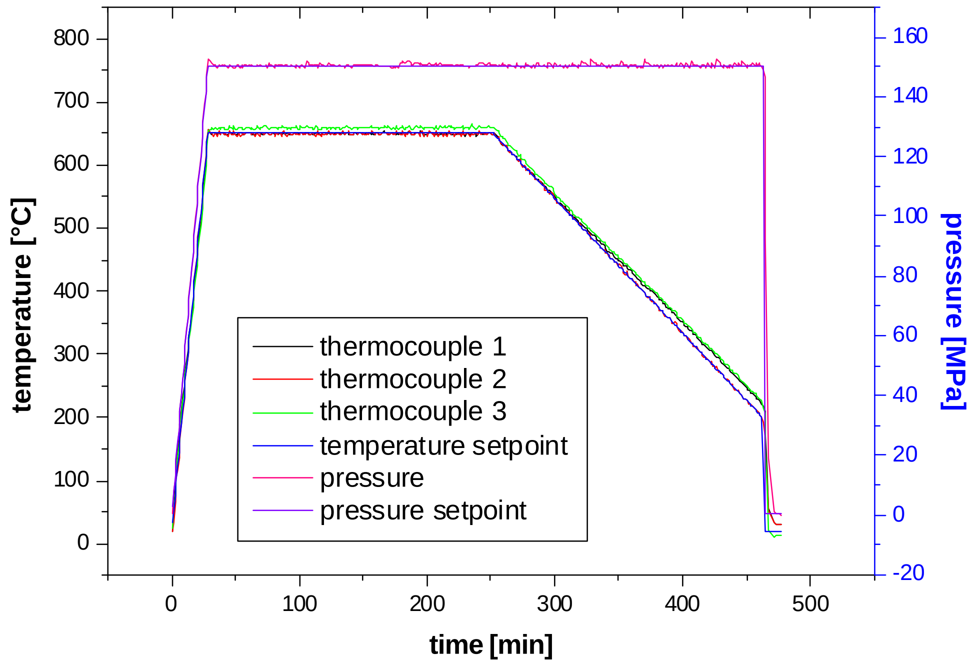
SCHOTT glass made of ideas

# Bulk relaxation experiments by Erlangen-Nürnberg, Clemson, Bayrisches Geoinstitut, SCHOTT VIII

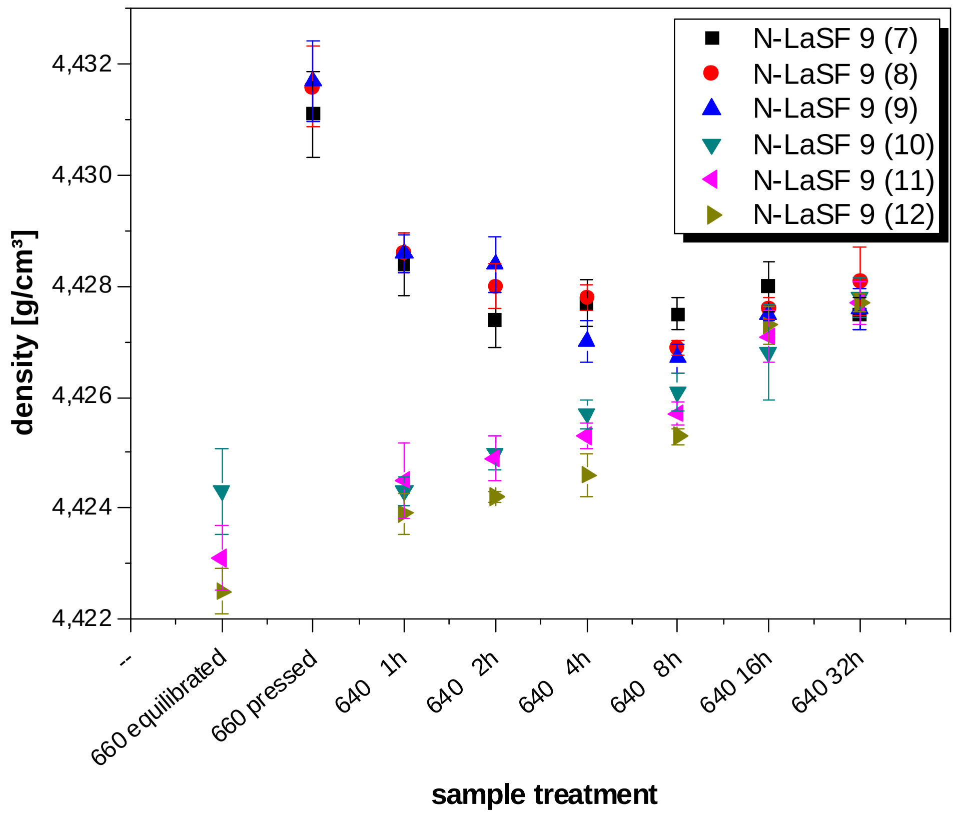
## Hot Isostatic Press experiments:

## - temperature and pressure load for N-LaSF9

## - time-dependent compliance of N-LaSF9




**Recorded data of HIP compression experiment for N-LaSF 9.**




**Density evolution over treatment time with change in fictive temperature $T_f$ of N-LaSF 9 (HIP) (compressed:7-9; reference: 10-12).**

# Bulk relaxation experiments by Erlangen-Nürnberg, Clemson, Bayrisches Geoinstitut, SCHOTT IX

## Results

Table 10: Table of stand. deviation in [%] of density increase obtained in this study.

| Glass | Pressure device | Increase in density [%] | Mean stand. error of density measurements | Mean stand. error in [%] of increase in density |
|---|---|---|---|---|
| K 7 | HIP | 0.34 | 1.4E-04 | 4 |
| | MAD | 9.52 | 7.5E-03 | 7.9 |
| N-BaF 10 | HIP | 0.30 | 2.4E-04 | 7.9 |
| | MAD | 7.23 | 9.6E-03 | 13 |
| N-LaK 12 | HIP | 0.16 | 2.5E-04 | 15 |
| | MAD | 3.74 | 8.7E-03 | 23 |
| N-LaSF 9 | HIP | 0.26 | 2.3E-04 | 8.9 |
| | MAD | 3.50 | 1.0E-02 | 29 |

Table 9: Comprehensive table of bulk moduli and compliances obtained in this study.

| | K 7 | | N-BaF 10 | | N-LaK 12 | | N-LaSF 9 | |
|---|---|---|---|---|---|---|---|---|
| | HIP | MAD | HIP | MAD | HIP | MAD | HIP | MAD |
| $K_0$ [GPa] | 40 | | 65 | | 68 | | 85 | |
| $K_\infty$ [GPa] | 21 | 23 | 28 | 33 | 39 | 45 | 35 | 53 |
| $K_\infty / K_0$ | 0.53 | 0.57 | 0.43 | 0.52 | 0.57 | 0.66 | 0.41 | 0.63 |
| $J(0)$ [$Pa^{-1}$] | 8.3E-12 | | 5.1E-12 | | 4.9E-12 | | 3.9 E-12 | |
| $J(\infty)$ [$Pa^{-1}$] | 1.6E-11 | 1.5E-11 | 1.2E-11 | 1.0E-11 | 8.5E-12 | 7.4E-12 | 9.6E-12 | 6.2E-12 |
| $J(\infty)/J(0)$ | 1.9 | 1.8 | 2.3 | 1.9 | 1.8 | 1.5 | 2.5 | 1.6 |
| $3J(0)$ [$Pa^{-1}$] | 2.5E-11 | | 1.5E-11 | | 1.5E-11 | | 1.2E-11 | |
| $3J(\infty)$ [$Pa^{-1}$] | 4.7E-11 | 4.4E-11 | 3.6E-11 | 3.0E-11 | 2.6E-11 | 2.2E-11 | 2.9E-11 | 1.9E-11 |