

Advanced Vitreous State – The Physical Properties of Glass



Dielectric Properties of Glass

Lecture 1: Dielectric in Static Field

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Resources

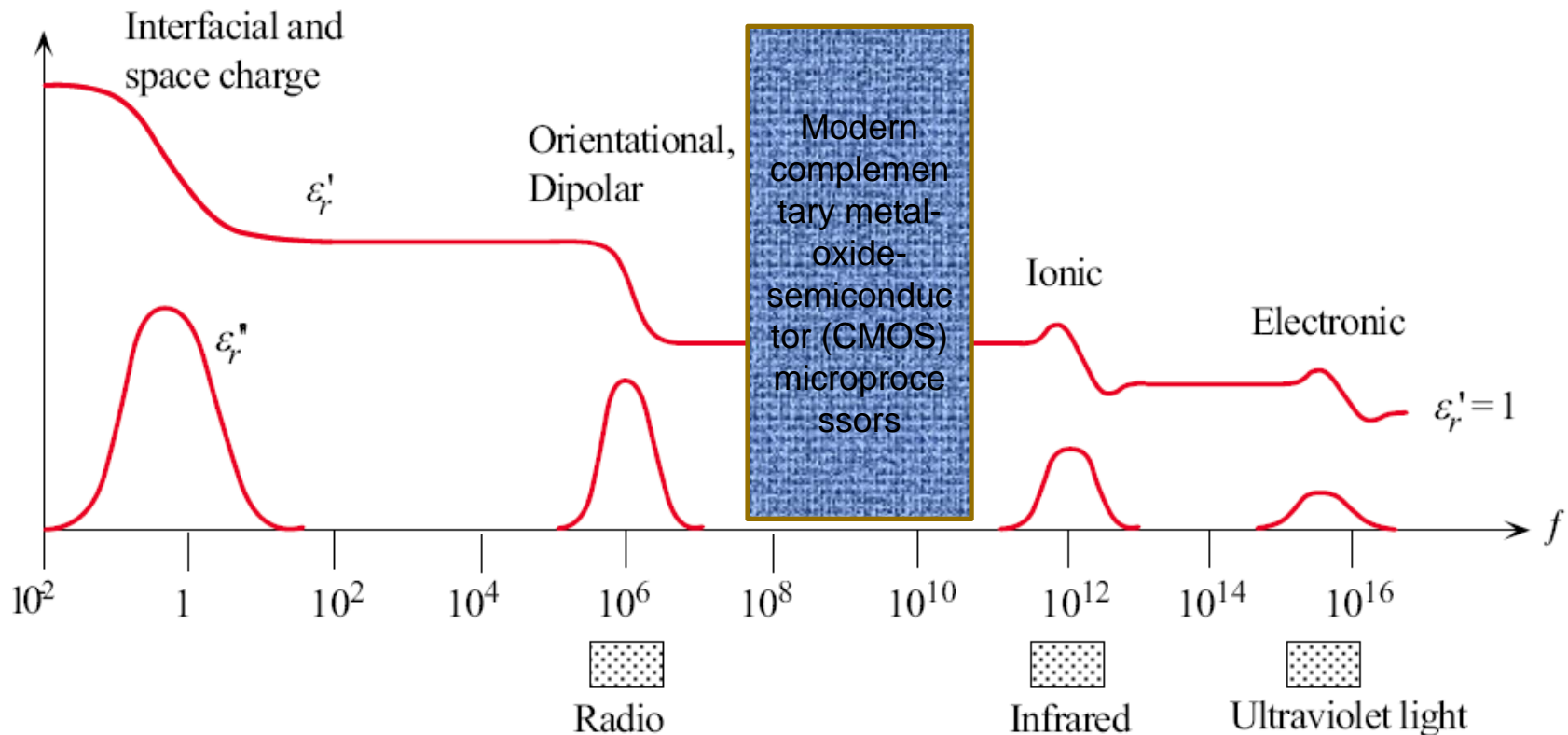
- Fundamental of Inorganic Glasses, A.K. Varshneya, Soc. Glass Tech, 2006
- *Principles of Electronic Materials and Devices by S. Kasap, 3rd Ed., McGraw Hill, 2006. Source of colored diagrams. Recommended for clear, concise description.*
- Dielectric and Waves, A.R. von Hippel, John Wiley, 1954
- Engineering Dielectrics, Vol. IIA, R. Batnikas and R.M. Eichhorn, eds. ASTM STP 783, 1983

What is a dielectric?

- Dia+electric i.e. poorly electric and can sustain electric field without appreciable current.
- **Uses:**
 - **Insulation for wires, cables, electrical equipment**
 - **Capacitors**
 - **Devices for propagation of e.m. waves**
 - (Piezoelectric transducers, time devices)
 - (Memory elements)
 - **Microelectronics**

Dielectrics in microelectronics:

- (a) Gate dielectrics, (b) Tunneling oxides in memory devices, (SiO_xN_y)
- (c) Capacitors, (d) Interconnect dielectrics, (e) Isolation dielectrics



Electronic and Ionic polarizations are most important.

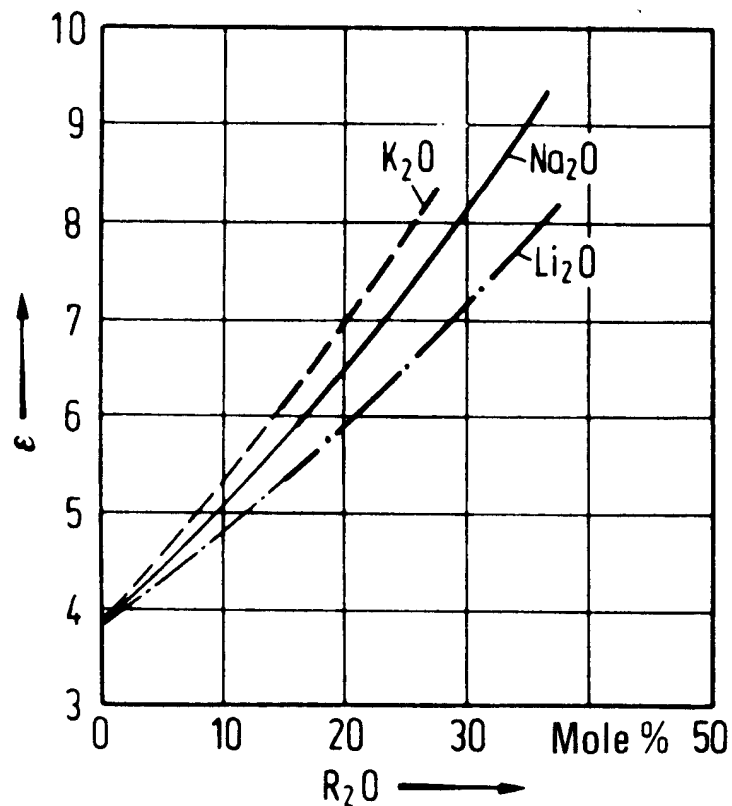
Principal Dielectric Properties: Why bother?

- 1. Dielectric constant, ϵ'
 - High for charge storage device e.g. capacitor, gate dielectric
 - Low for faster signal transmission (speed $\sim 1/\sqrt{\epsilon}$)
- 2. Dielectric (energy) loss, ϵ''
 - High for microwave heating
 - Low for signal transmission
- 3. Dielectric breakdown
 - High for most insulating applications e.g. tunneling oxides
 - Low for fuses (?)

Rigid insulators: glass, ceramics, porcelain, epoxies..

- Advantages of glass & ceramics over polymers
 - Superior dielectric properties
 - No creep or deformation at RT
 - Greater stability in hostile environment
- Other desirable characteristics
 - Suitable thermal and mechanical properties
 - Ability to form seals with metals/ceramics
 - No porosity

How can we understand this?



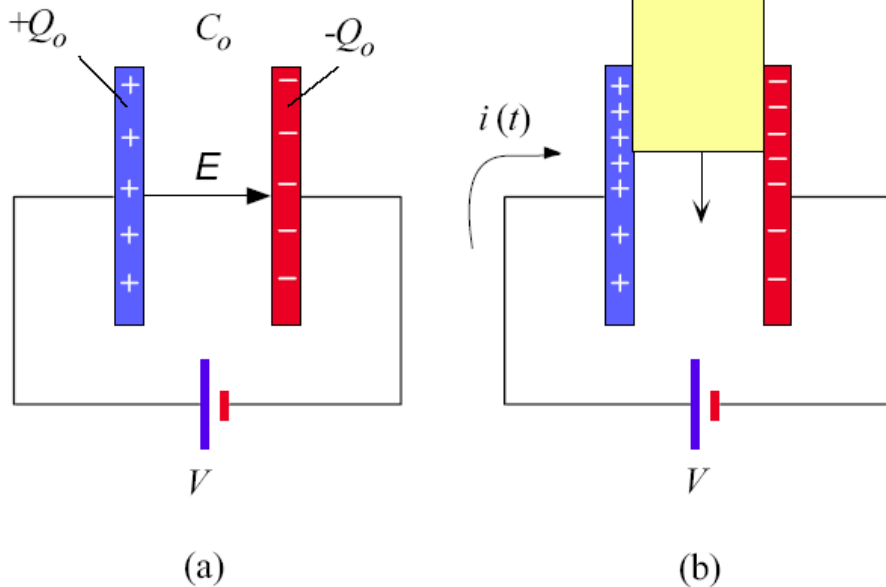
- ❖ Note that the addition of alkali oxide to silica increases the MHz-GHz frequency dielectric constant monotonically.
- ❖ The increase is higher for the larger alkali.

FIGURE 154. Dielectric constant ϵ of binary alkali silicate glasses at $4.5 \cdot 10^8$ Hz and room temperature, from Appen and Bresker [26].

Dielectric in static (dc) field

$$Q_o \propto V$$

$$= C_o V$$



Q_o = charge on the plates

V = voltage

C_o = capacitance of a parallel plate capacitor in free space.

Units: Coulomb/Volt = Farad

(a) Parallel plate capacitor in vacuum.

(b) As a slab of insulating material is inserted between the plates, there is an external current flow indicating that more charge is stored on the plates.

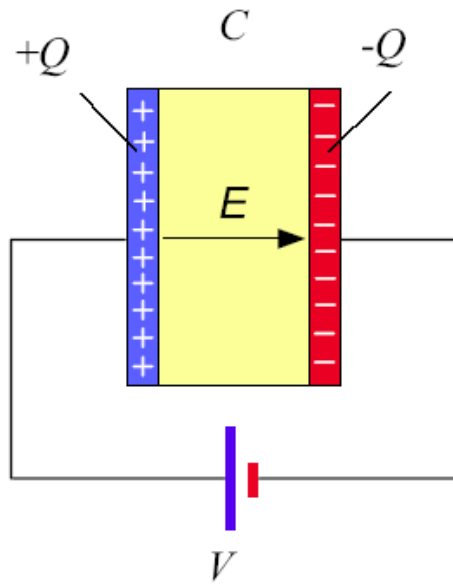
$$C_o \propto \text{Area of plates (neglect edge effect)}$$

$$\propto 1/\text{separation between the plates}$$

$$= \epsilon_0 A/d$$

$$\epsilon_0 = 8.854 \times 10^{-12} \text{ F/m}$$

Capacitance of a dielectric



$$\epsilon_r = \frac{Q}{Q_0} = \frac{C}{C_0}$$

ϵ_r = relative permittivity,

Q = charge on the plates with a dielectric medium $> Q_0$

So that $C > C_0$ and $\epsilon_r > 1.0$

Goal: Understand the origin of ϵ_r and manipulate its value by material design.

Coulomb's law and electric field

Force between two charges in vacuum:

$$\mathbf{F}_0 = q_1 q_2 / 4\pi\epsilon_0 r^2$$

Coulomb's law – Proven to better than 2 ppb

Electric field in vacuum, $\mathbf{E}_0 = q_1 / 4\pi\epsilon_0 r^2$

Force between two charges in dielectric:

$$\mathbf{F} = q_1 q_2 / 4\pi\epsilon_0 \epsilon_r r^2$$

Electric field in dielectric, $\mathbf{E} = q_1 / 4\pi\epsilon_0 \epsilon_r r^2$

The field in dielectric is reduced by ϵ_r .

The dielectric is not neutral, but must have non-uniform charge \Rightarrow charges are shifted as the dielectric gets polarized.

Displaced charge produces electrical force given by displacement vector

$\mathbf{D} = \epsilon_0 \epsilon_r \mathbf{E}$, so that in general ϵ_r is a tensor (of course, scalar for glass).

Dielectric constant is a macroscopic/engineering property!

Polarization in general!

← Macro

Former President Bill Clinton warned Saturday that the country is becoming increasingly polarized despite the historic nature of the Democratic primary.



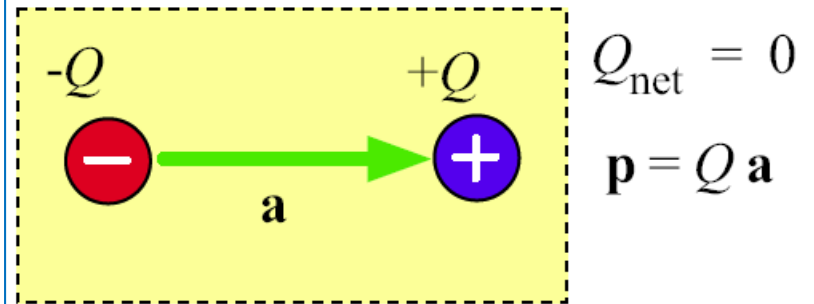
← Micro

Microscopic view:

The simplest unit of polarization:
Dipole, where positive charge is displaced with respect to its countercharge.

Define dipole moment:

\mathbf{p} = charge x **separation** (-Q to +Q)



Define polarization \mathbf{P} = dipole moment / volume

For small fields: $\mathbf{p} \propto \mathbf{E}_{\text{loc}}$ or $\mathbf{p} = \alpha \mathbf{E}_{\text{loc}}$, where α is polarizability and \mathbf{E}_{loc} is local electric field acting on the specific dipole.

If there are N dipoles/vol, $\mathbf{P} = N\mathbf{p} = N\alpha \mathbf{E}_{\text{loc}}$

Dielectric susceptibility, χ

Experimentally, $\mathbf{P} \propto \mathbf{E}$,
 so that $\mathbf{P} = \chi \mathbf{E}$
 χ is dielectric susceptibility;
 describes the bulk response of
 the material.

Two sources of charge on the plates:

- (i) Charge from connection to the battery
- (ii) Charge induced by the bound charge from the polarization of the dielectric. This *bound* surface charge/area = P

$$\mathbf{D} = \mathbf{D}_0 + \mathbf{P} = \epsilon_0 \mathbf{E} + \chi \mathbf{E}$$

$$\text{Also } \mathbf{D} = \epsilon_0 \epsilon_r \mathbf{E}$$

$$\text{So that } \chi = \epsilon_0 (\epsilon_r - 1)$$

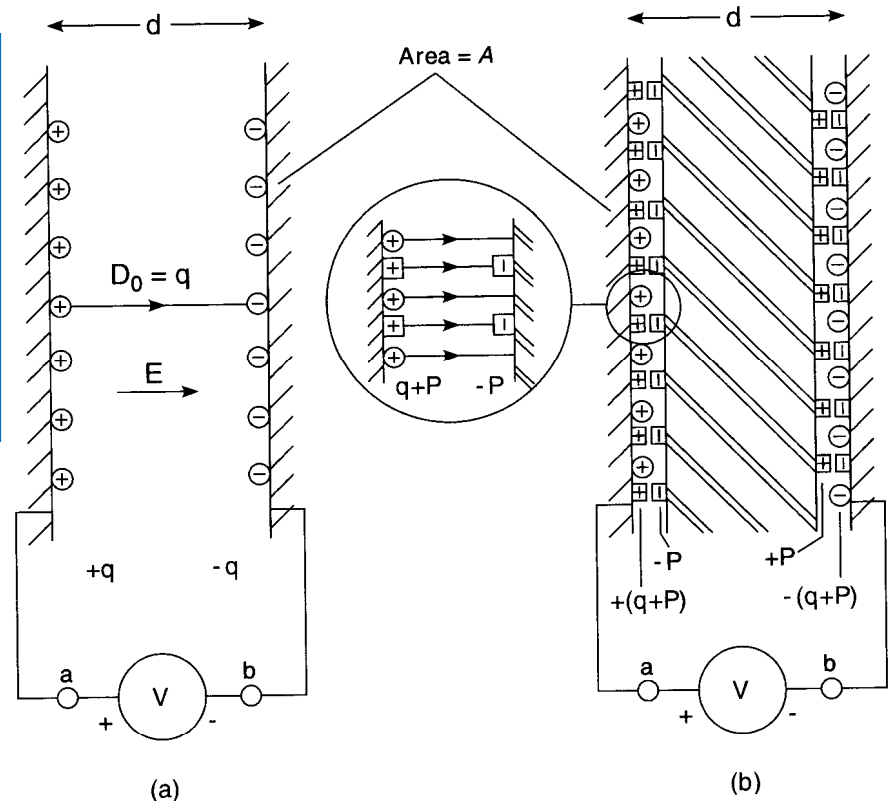
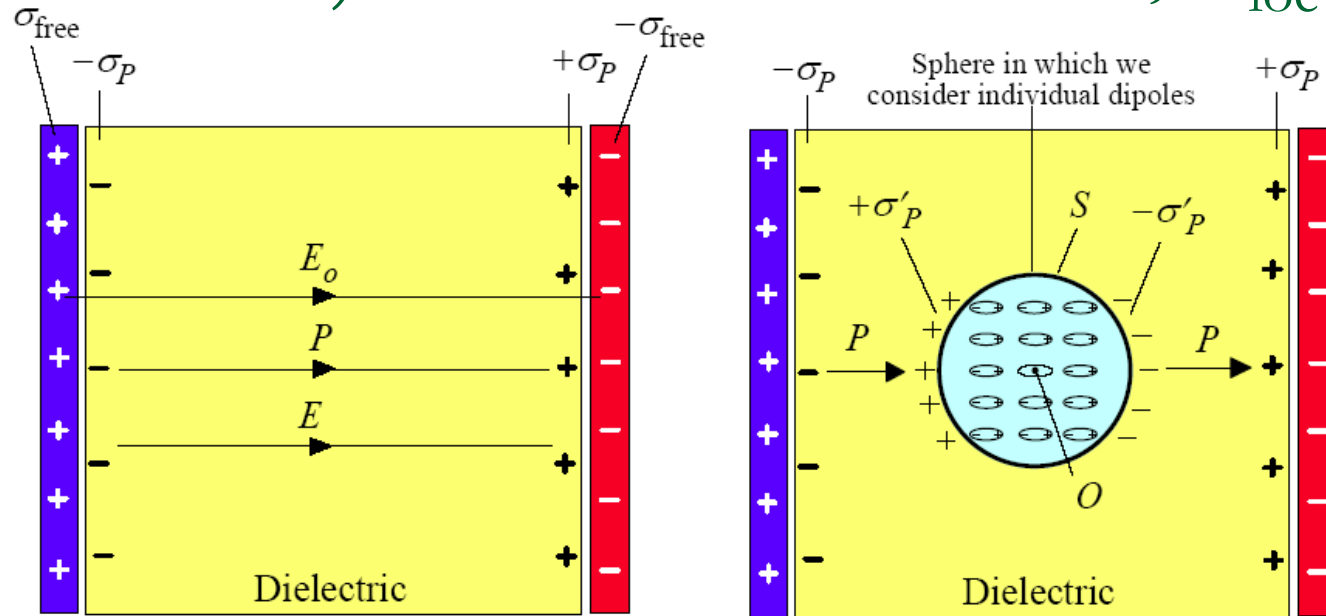


Figure 15-1. (a) A parallel plate capacitor connected to a potential difference V . With vacuum between the plates, the electric displacement is $D_0 (= \text{charge } q)$. The flux lines start from the $+$ charges on the positive plate and end on the $-$ charges on the negative plate. (b) Upon introducing a dielectric between the plates, polarization charges $+/-P$ appear on the dielectric facing the plates. This causes the charges on the plates to become $(q+P)$ and $-(q+P)$. Inset shows exaggeration of the plate–nearest dielectric face region. (Adapted after B. K. P. Scaife, *Principles of Dielectrics*,

Local (or Lorenz) electric field in a solid, E_{loc}



$$E_{loc} = E + E_{spherical\ cavity} + E_{dipoles}$$

Zero for cubic crystals and glasses

$$E_s = \frac{1}{3\epsilon_0} P$$

So that local or Lorenz field, $E_{loc} = E_{ext} + P/3\epsilon_0 = E_{ext} (\epsilon_r + 2)/3$

$$P = N\alpha E_{loc} = \epsilon_0(\epsilon_r - 1)E_{ext}$$

Claussius Mossotti Eq.
Micro ↔ Macro

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{N\alpha}{3\epsilon_0}$$

Polarization Mechanisms

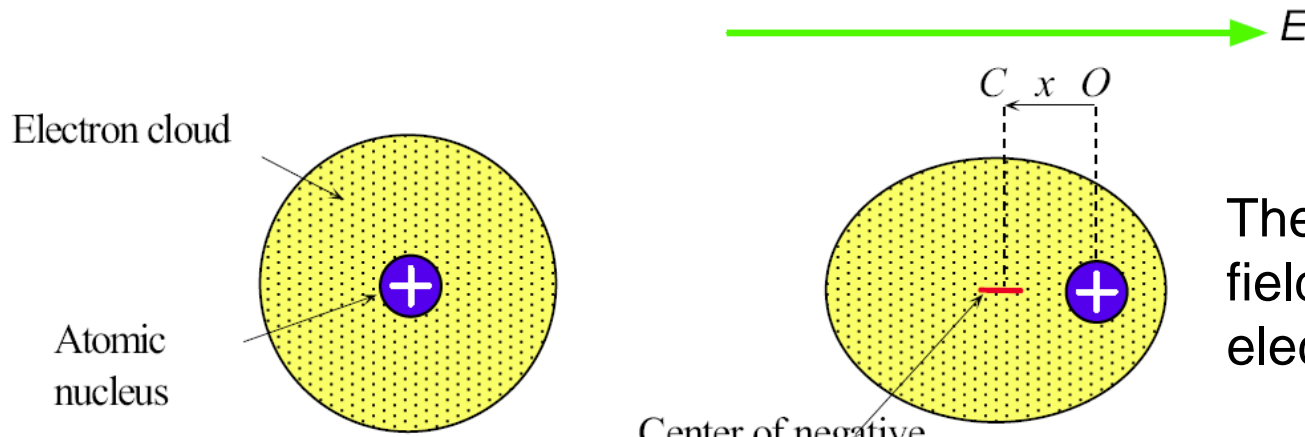
1. Electronic polarization
2. Ionic/atomic polarization
3. Dipolar/orientational polarization
 - a) 'Jellyfish' polarization
4. Interfacial polarization

Nature has two types of processes: relaxation or resonance.

1 and 2 are resonance processes

3 and 4 are relaxation processes

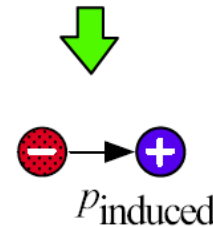
Electronic polarizability of an atom, α_e



(a) A neutral atom in $E = 0$.

The force due to applied field pulls the nucleus and electron cloud apart.

In equilibrium, it is balanced by the Coulombic attraction between them.



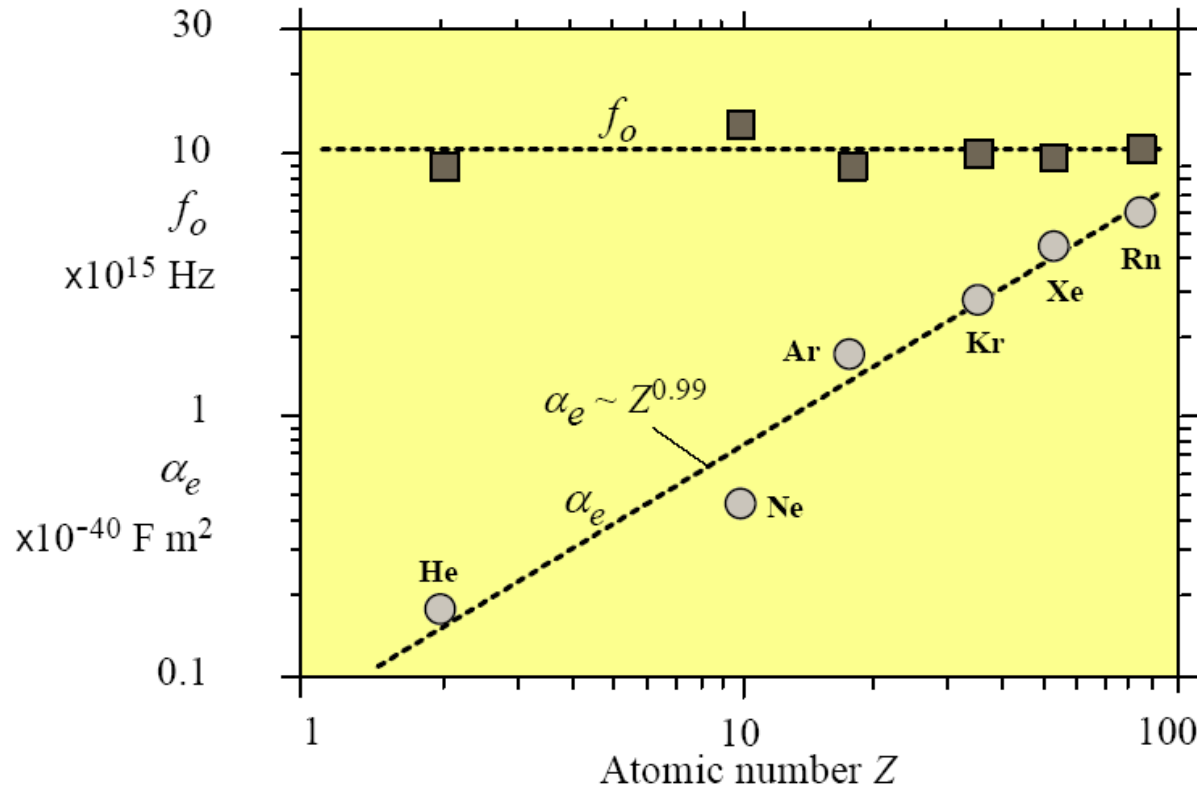
The *induced* electronic dipole moment

$$p_e = (Ze)x = \left(\frac{Z^2 e^2}{\beta} \right) \mathcal{E}$$

$Z = \#$ of electrons in the atom, $x =$ distance between the nucleus and the center of negative charge, $\beta =$ constant, $\mathcal{E} =$ electric field

<http://hypertextbook.com/physics/electricity/dielectrics/stretching.html>

Electronic polarizability of inert gas $\sim Z$



When E is removed, the electron cloud will return, and oscillate with its natural frequency $\omega_0 = 2\pi f_0$

$$\alpha_e = \frac{Ze^2}{m_e \omega_o^2}$$

$$\omega_o = \left(\frac{\beta}{Zm_e} \right)^{1/2}$$

- $\alpha_e \propto Z$. Its resonance freq. (in UV) is \sim independent of Z.
- α_e is $\sim T$ independent.

Use high Z elements to increase refractive index of a glass.

Electronic polarizability

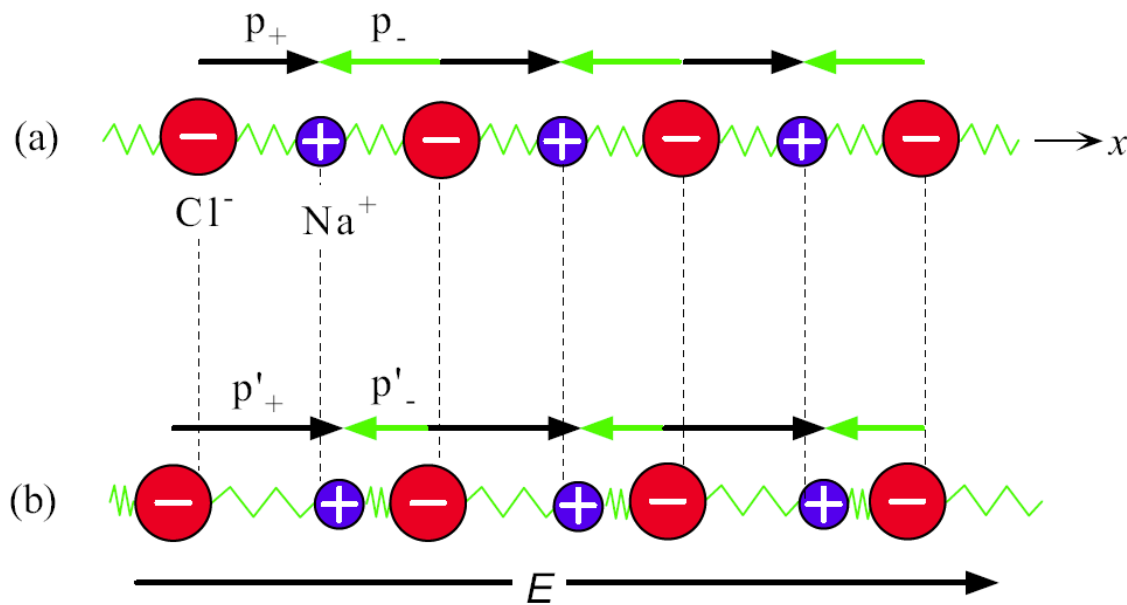
General remarks - ***tips for material design***:

- α_e determines n in the visible region, and at lower freq.
- **In a given column α_e increases with atom radius.**
- **α_e for anions \gg for cations.**

						He(0.201)
Li ⁺ (0.029)	Be ⁺² (0.008)	B ⁺³ (0.003)	C ⁺⁴ (0.001)	O ⁻² (3.88)	F ⁻ (1.04)	Ne(0.39)
Na ⁺ (0.179)	Mg ⁺² (0.094)	Al ⁺³ (0.052)	Si ⁺⁴ (0.016)	S ⁻² (10.2)	Cl ⁻ (2.95)	Ar(1.62)
K ⁺ (0.83)	Ca ⁺² (0.47)	Sc ⁺³ (0.286)	Ti ⁺⁴ (0.185)	Se ⁻² (10.5)	Br ⁻ (4.77)	Kr(2.46)
Rb ⁺ (1.40)	Sr ⁺² (0.86)	Y ⁺³ (0.55)	Zr ⁺⁴ (0.37)	Te ⁻² (14.0)	I ⁻ (7.10)	Xe(3.99)
Cs ⁺ (2.42)	Ba ⁺² (1.55)	La ⁺³ (1.04)	Ce ⁺⁴ (0.73)			

Note: Above α_e values are by Pauling and Tessman et al. Others have given different values, depending on the compositions used for self-consistency (see Kittel, p.391).

Ionic polarizability, α_i



1-d NaCl crystal:

Without E, net dipole moment is 0.

With E, cations and anions move in opposite direction, producing net polarization.

$$P_i = N_i \alpha_i E_{loc}$$

- ❖ α_i depends on the bonding between cation and anion – more difficult to model when bonding is complex as in solids with mixed bonding.
 - ❖ α_i is also $\sim T$ independent (if structure does not change).
 - ❖ ω_0 is in the IR – why?
- It depends on reduced ion mass (μ) $\ll m_e$ (also bonding).

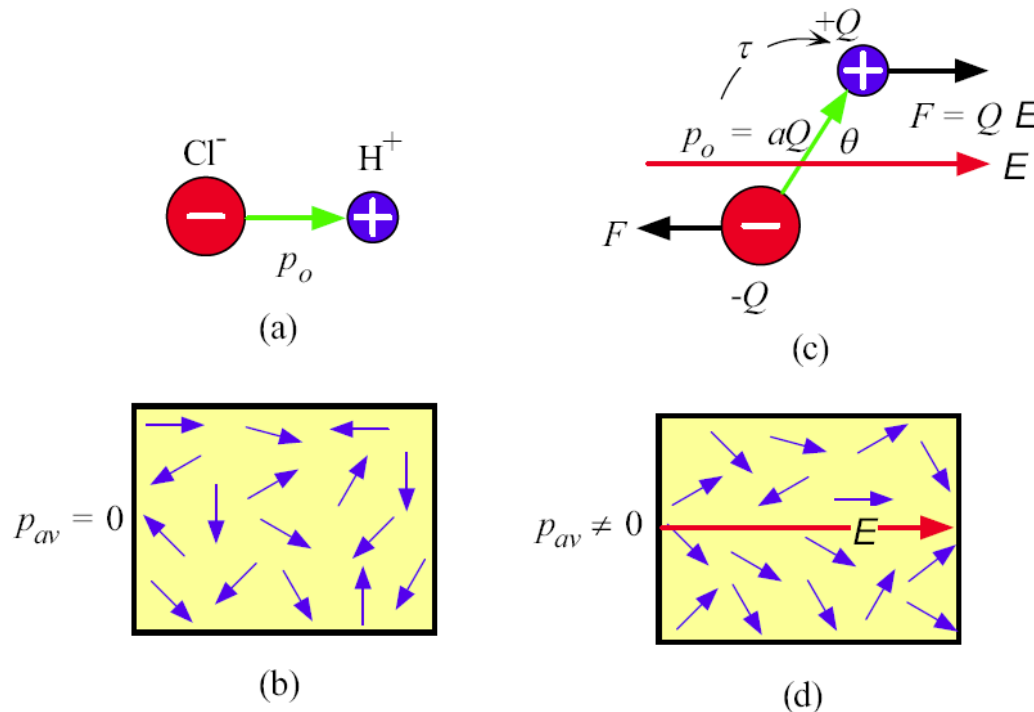
High (but <optical) frequency dielectric constant

At frequencies below the resonance of ionic polarization, both electronic and ionic polarizations will contribute to dielectric constant. Claussius Mossotti equation gives for glass.

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{1}{3\epsilon_o} (N_e \alpha_e + N_i \alpha_i)$$

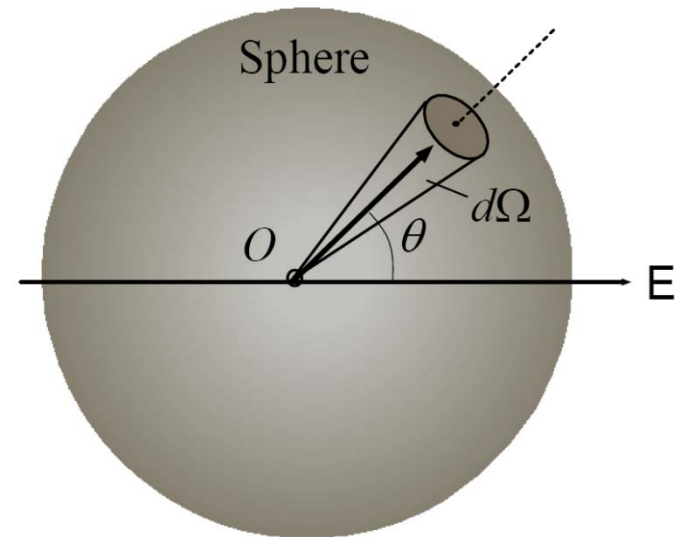
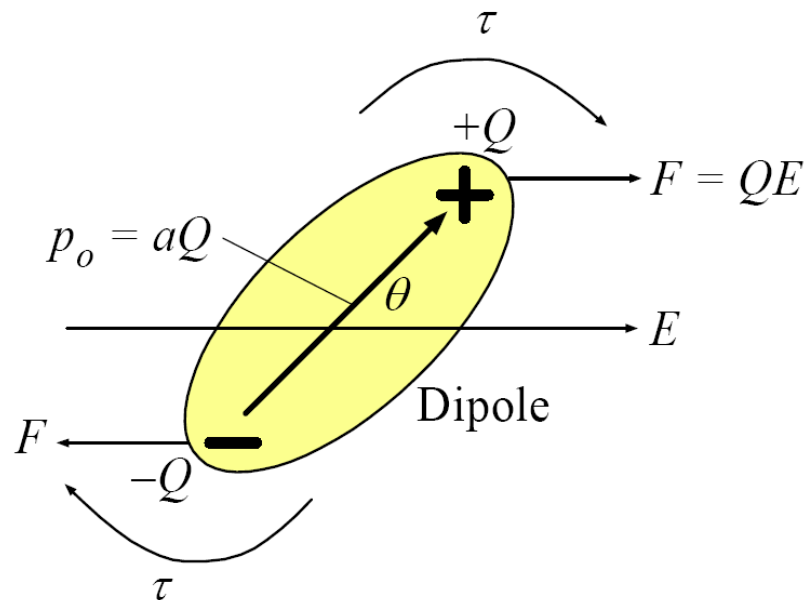
Additional mechanisms like dipolar, interfacial and interfacial polarization may also contribute.

Dipolar/orientational polarization of a polar gas



- ❖ A gas of permanent dipoles has zero polarization due to their random orientation.
- ❖ In \mathbf{E} , dipoles feel a torque that tries to align the dipoles parallel to \mathbf{E} , which is balanced by thermal agitation. The result is a net dipole moment that **↑ or ↓ as $T \uparrow$?**
- ❖ **$P \downarrow$ as $T \uparrow$**

Dipoles in a field

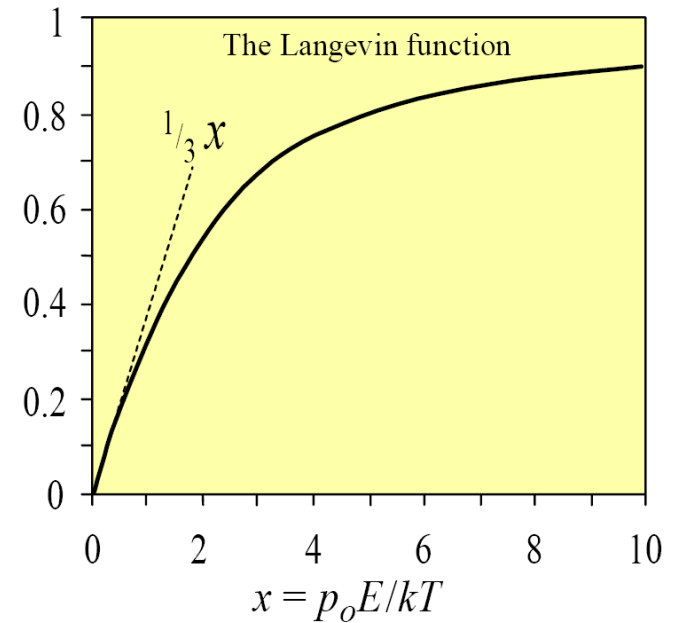


$$\text{Energy of a dipole} = \mathbf{p}_0 \cdot \mathbf{E} = p_0 E \cos \theta$$

Average orientational polarization of polar gas

$$P_{av} = \frac{\int_0^{4\pi} (p_o \cos \theta) \exp(-p_o E \cos \theta) d\Omega}{\int_0^{4\pi} \exp(-p_o E \cos \theta) d\Omega}$$

Dipole moment along E



Integration gives a Langevin function $L(x)$

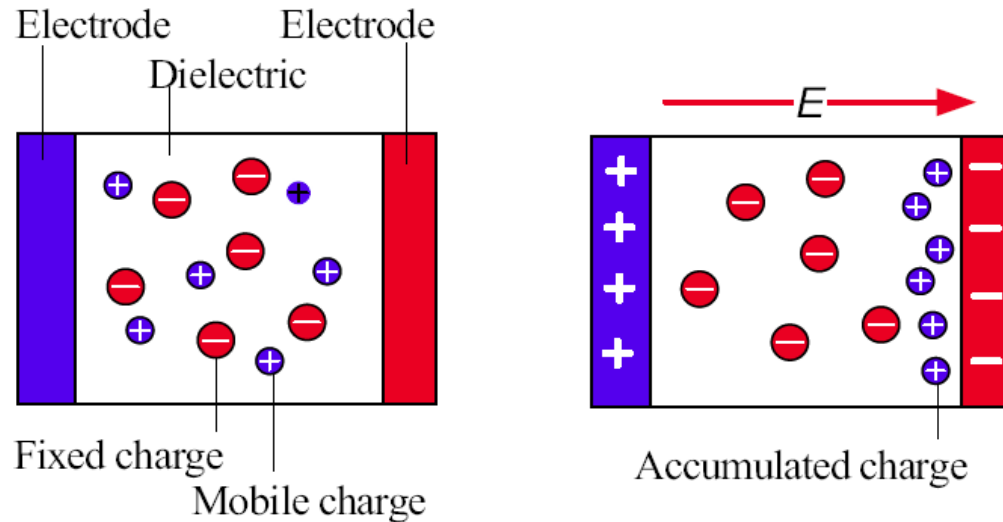
$$p_{av} = p_o L(x) = p_o \coth(x - 1/x); \text{ where } x = p_o E / kT$$

At low E , typical of common use, $L(x) = x/3$. Then,

$$p_{av} = p_o^2 E / 3kT \text{ or}$$

$$\alpha_{\text{dipolar}} = p_o^2 / 3kT$$

Interfacial polarization



In the presence of an applied field, the mobile positive ions migrate toward the negative electrode and collect there leaving behind negative charges in the dielectric. The dielectric therefore exhibits interfacial polarization. Since it arises from the migration of charge to much larger distances, the polarization is orders of magnitude larger than from other mechanisms.

Glasses do not have interfaces \Rightarrow Not an important mechanism for glass. However, glasses are often ionic conductors. So interfacial polarization will develop if the charge carrier can not **??** [freely exchange at the electrodes.](#)

Dielectric constant of oxide glasses

- ❖ Oxygen, being the anion, is most easily polarized.
- ❖ Non-bridging oxygen is even more polarizable than bridging oxygen.
- ❖ With decreasing field strength of the modifier cation, the M^+ - NBO^- bond can be polarized more easily. The same trend is observed with alkaline earth cations.

Calculation of dielectric constant from composition

Often dielectric constant is additive, and therefore can be estimated from composition (when structural changes are small or monotonic). The Table is for ϵ_r at RT and 0.45 GHz, as obtained by Appen & Bresker (1952) .

$$\epsilon = \frac{1}{100} \sum \epsilon_i p_i,$$

p_i is mole% of i^{th} component

From Glass by H. Scholze

Oxide	Factor
Li ₂ O	14.0 (15.0) ^a
Na ₂ O	17.6 (17.6) ^a
K ₂ O	16.0 (20.3) ^a
BeO	13.8
MgO	15.4
CaO	17.4
SrO	18.0
BaO	20.5
B ₂ O ₃	3 ... 8 ^b
Al ₂ O ₃	9.2
SiO ₂	3.8
TiO ₂	25.5
ZnO	14.4
CdO	17.2
PbO	22.0
MnO	13.8
FeO	16.0
CoO	15.2
NiO	13.4

^aThe values in parentheses are valid for the binary R₂O—SiO₂ glasses.

^bThe factor of B₂O₃ is dependent on the glass composition.

Dielectric constant of $\text{Na}_2\text{O} \cdot x\text{Al}_2\text{O}_3 \cdot (3-2x)\text{SiO}_2$

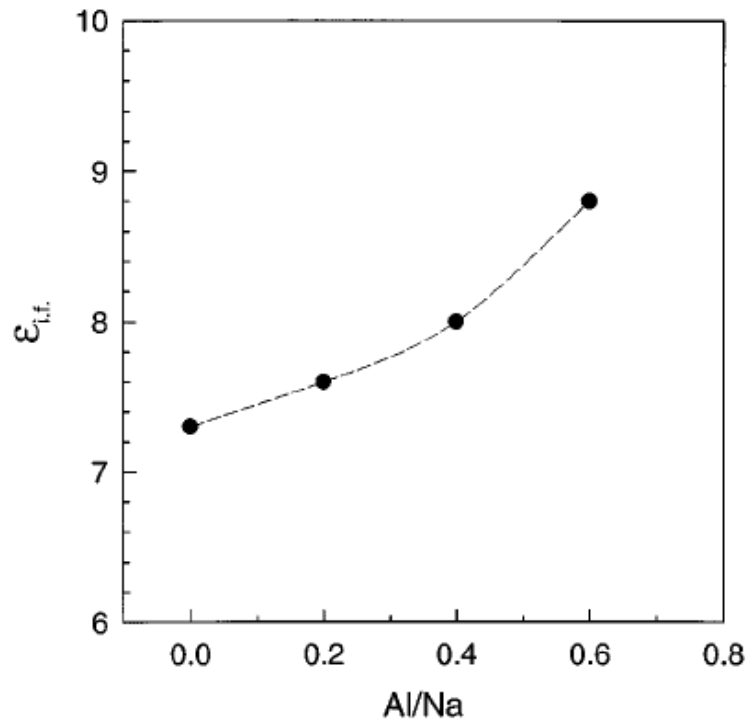


FIG. 4. Intermediate-frequency dielectric constant of the SAS glasses at 25 °C.

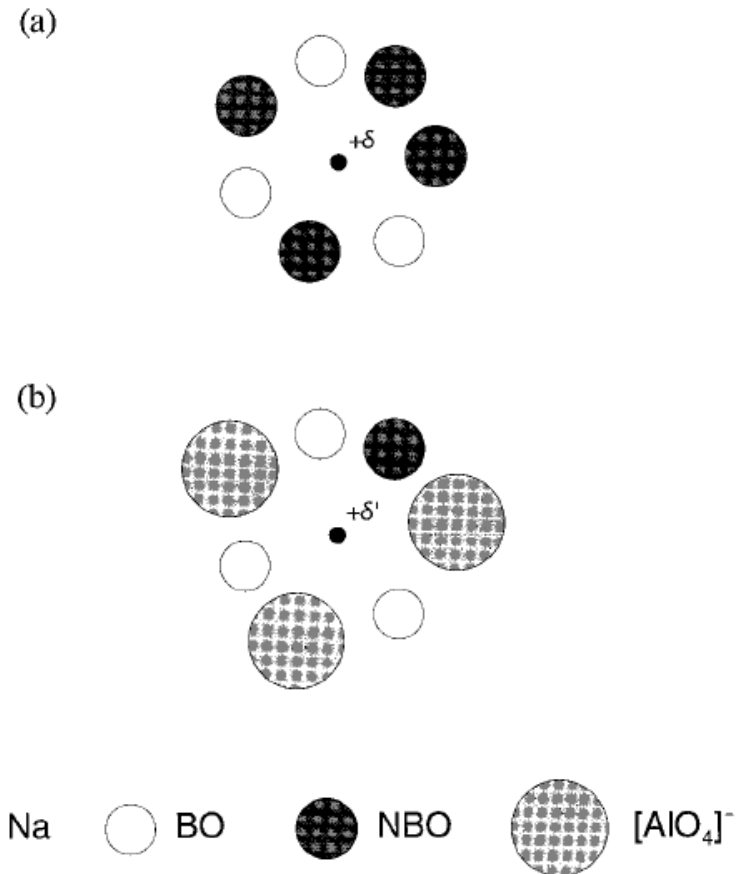


FIG. 7. Environment of a sodium ion consisting of: (a) bridging and non-bridging oxygen atoms in sodium trisilicate glass, and (b) bridging and nonbridging oxygen atoms as well as aluminum tetrahedra in SAS glass. δ and δ' are charges on sodium ions in respective glasses with $\delta' > \delta$.

Hsieh, Jain, Kamitsos, J Appl Phys (1996)

Structural origin of ϵ_r of oxide glasses

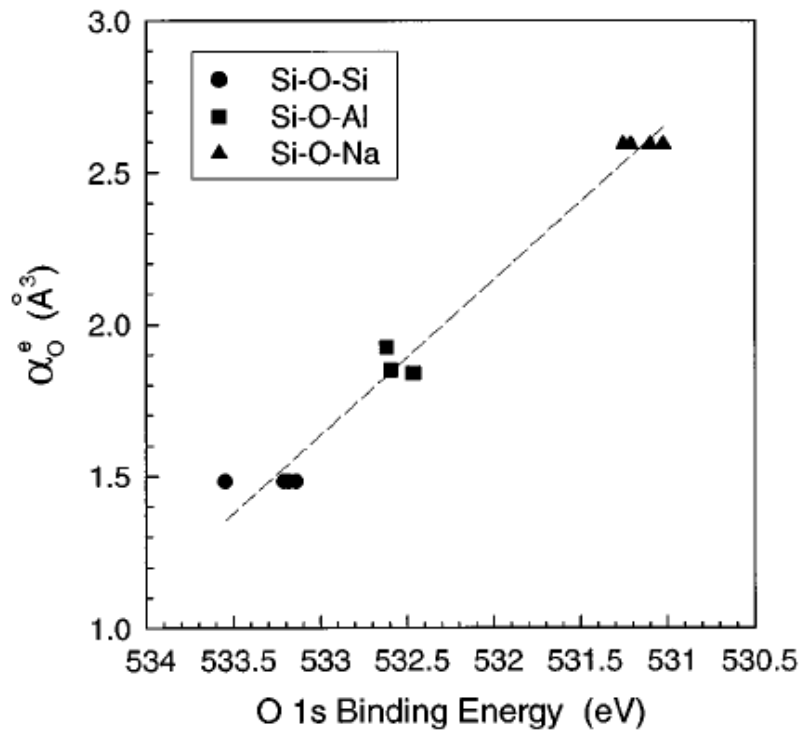


FIG. 8. Correlation between the electronic polarizability of oxygen ions and the O 1s XPS binding energy in the SAS glasses.

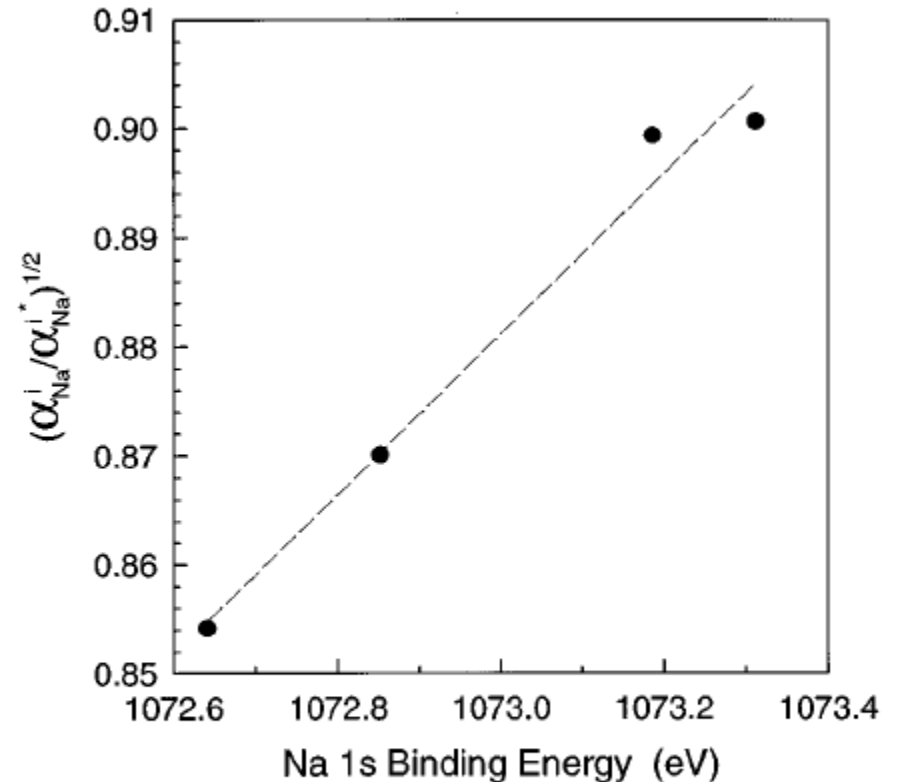


FIG. 9. Correlation between the ionic polarizability of sodium ions and the Na 1s XPS binding energy in the SAS glasses.

Why is this polar bear worried?



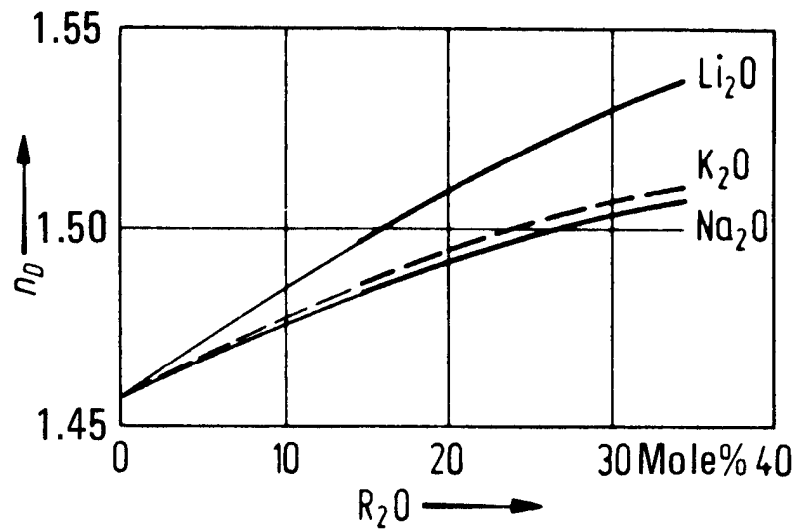


FIGURE 102. Indexes of refraction n_D of binary alkali silicate glasses, from various authors.

Local field in a dielectric, E_{loc}

Fig. 18.3 Kingery??

$$E_{loc} = E_{ext} + E_1 + E_2$$

Field due to spherical cavity, $E_1 = P/3\epsilon_0$

Field due to individual dipoles, $E_2 = \text{zero}$ for glass with random distribution

$$\text{Local or Lorenz field, } E_{loc} = E_{ext} + P/3\epsilon_0 = E_{ext} (\epsilon_r + 2)/3$$

$$\text{Claussius-Mossotti Eq. } \alpha = (3\epsilon_0 / N) (\epsilon_r - 1)/(\epsilon_r + 2)$$