Electronic and ionic relaxations in oxide glasses

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OUTLINE

1. Electronic conductivity in transition metal oxide (TMO) glasses
   - data presentation
   - interpretation

2. Mixed electronic-ionic conducting glasses
   Classification of TMO glasses containing alkali ions:
   - TMO is a glass forming oxide
   - TMO is a glass modifier.

3. Internal friction
   - a powerful technique of mechanical spectroscopy for the
   study of relaxation processes in glasses
Glass containing a high concentration of transition metal ions are *electronic conductors* with the conductivities in the range $10^{-4}$ to $10^{-12}$ S/cm at 300 K and a negative coefficient of resistivity. This classifies them as a form of amorphous semiconductors.

**Typical glass forming oxides:**

$\text{SiO}_2$, $\text{B}_2\text{O}_3$, $\text{P}_2\text{O}_5$, $\text{GeO}_2$, $\text{TeO}_2$,

**Typical transition metal oxide (TMO):**

$\text{V}_2\text{O}_5$, $\text{FeO}$, $\text{Fe}_2\text{O}_3$, $\text{CuO}$, $\text{Cu}_2\text{O}$, $\text{WO}_3$, $\text{MoO}_3$

The loss of oxygen from the melt produces a lower valency state of transition metal ion.

*For example:*

$$\text{V}^{5+} \xi \text{V}^{4+} \quad \text{Fe}^{3+} \xi \text{Fe}^{2+}$$

$$\text{Cu}^{2+} \xi \text{Cu}^{+} \quad \text{W}^{6+} \xi \text{W}^{5+}$$

Electrical conduction occurs by an electron hopping from an ion of the low valency state ($\text{V}^{4+}$) to an ion of high valency state ($\text{V}^{5+}$). The number of current carrier $N$ is of the order of transition ions concentration ($-\text{V}^{4+}$). $N \cdot 10^{20}$ cm$^{-3}$ and is constant.

The mobility calculated from conductivity is very low, generally below $10^{-4}$ cm$^2$/Vs. In this case the interaction is strong enough to form *small polarons*. 
**Polaron formation**

Excess electron displaced lattice atoms or ions forming polaron

Displaced atoms provide a potential well that differs from that produced by undisplaced atoms. The electron’s energy decreases by the self-trapping energy $E_S$. If the potential well is sufficiently deep, the carrier may occupy a bound state. In this case the excess charge cannot escape from its position without an alteration of the position of the surrounding atoms.

*The polaron is the entire unit comprising the self-trapped carrier and the atomic displacement pattern*
DC CONDUCTIVITY

On the basis of a simple diffusion model, Mott, has proposed an equation for dc conductivity in TMO glasses:

\[
\sigma = C(1 - C) \frac{e^{2\nu_{el}}}{RkT} \exp(-2aR) \exp\left(-\frac{W}{kT}\right)
\]

where \(\alpha\) is the rate of the wave function decay, \(\nu_{el} \cdot 10^{15} \text{ s}^{-1}\) is the electronic frequency, 
C is the ratio of ion concentration in the low valency state to the total concentration of transition metal ions e.g. Fe\(^{2+}\)/Fe\(_{\text{tot.}}\), R is average site spacing. This equation can be compared to the common Arrhenius formula: \(\sigma = \sigma_0 \exp(-W/kT)\) where preexponential factor is:

\[
\sigma_0 = C(1 - C) \frac{e^{2\nu_{el}}}{RkT} \exp(-2aR)
\]

In the low temperature range (below the Debye temperature) the activation energy decreases with decreasing temperature. This behaviour is attributed to the reduced electron-phonon interaction.
Temperature dependence of dc conductivity in a typical transition metal oxide glasses
Arrhenius diagram of conductivity for various glasses:
1. AgPO₃-AgI, 2. Ag₂MoO₄-AgI, 3. AgPO₃-AgBr, 4. GeS₂-GeS-AgI,
5. AgAs₂S₃-Ag₂S, 6. GeS₂-Li₂S, 7. LiTaO₃, 8. B₃O₃-Li₂O-LiCl,
In electronic conducting glasses

impedance spectroscopy = ac conductivity

*Impedance spectrum in a typical iron-phosphate glass*
The frequency dependent conductivity can be divided into two domains, one where the absolute magnitude of ac conductivity is close to the dc conductivity, and another where the absolute magnitude of ac conductivity is larger than dc conductivity.

The conductivity as a function of frequency in a typical iron-phosphate glass for different temperatures.

The dependence of the ac electrical conductivity $\sigma$ on angular frequency $\omega$ is found to obey the form:

$$\sigma(\omega) = \sigma(0) + A\omega^{s(T)}$$

where $\sigma(0)$ is the dc conductivity and the exponent $s(T)$ is in the range $0.4 < s < 1$. The universality of such power-law behaviour for many different classes of materials was pointed out by Jonscher, who referred it as a "universal dynamic response" (UDR).
Discharge current versus time in a typical iron-phosphate glass

Dielectric loss factor vs frequency obtained from transformation of discharge current into the frequency domain
As shown in this Figure, the activation energy of the dc conductivity and the frequency of dielectric loss peaks is the same.

The BNN relation $\sigma = 2\pi f_{mD}(\Delta g - g_s)p$ is obeyed in $50\text{P}_{2}\text{O}_5-(50-x)\text{FeO}-x\text{MO}$ ($x=\text{Ca,Ba}$) for $p=1$ and $\Delta g = g - g_s = 17.6 \div 18.7$ (M=Ba); 11.4-13.4 (M=Ca)
INTERPRETATION

Theories, models of ac conductivity in electronic conducting glasses

Austin and Mott  1969
  Long   1982
  Elliott 1987
  Dyre   1988
  Hunt    1991
Funke and Roling 1996
The Hunt theory

The Hunt theory distinguishes two frequency ranges: at high frequency electrons (or ions) jumps forth and back between sites. This is the pair-hopping regime, which yields to the following expression for conductivity:

$$\sigma_i(\omega) = \sigma_{dc} \left[ 1 + A \left( \frac{\omega}{\omega_m} \right)^s \right]$$

where $s < 1$ and $A$ is a constant which depends on the type of pair approximation relevant in the network. The cross-over frequency is the frequency of peak $\omega_m$, at which the individual (parallel) pair processes percolate and that cause the appearance of series processes. The series processes in the low frequency range are non-local and can be treated as percolation of individual particles over macroscopic distances in clusters or chains. For $\omega < \omega_m$ a fractal structure of clusters is responsible for relaxation currents and the conductivity has a form:

$$\sigma_i(\omega) = \sigma_{dc} \left[ 1 + K(d) \left( \frac{\omega}{\omega_m} \right)^r \right]$$

where $r = 1 + d - d_f > 1$; $d$ is the dimensionality of the space containing relevant clusters and $d_f$ is the fractal dimensionality of such clusters. $K(d)$ is a dimensionally dependent constant related to the statistics of the contributing clusters.

According to Hunt, in the pair-hopping regime the ac part is:

$$\sigma_{ac} = \sigma_{dc} A (\omega/\omega_m)^s$$

From BNN relation we have: $\omega_m = \sigma_{dc} g / \Delta g$ and the result obtained for $\sigma_{ac}$ is:

$$\sigma_{ac} = A (\omega \varepsilon_0 \Delta \varepsilon)^s \sigma_{dc}^{1-s}.$$  

This equation implies that in log-log scale $\sigma_{ac} = f(\sigma_{dc})$ should be linear with a slope of $(1-s)$.  


The ac conductivity, $\sigma_{ac}$, for $s=0.7$ as a function of DC conductivity, $\sigma_{dc}$, in different TMO glasses: $x$, $P_2O_5-V_2O_5-MO$ ($M=Mg, Ca, Sr, Ba$); $\square$, $P_2O_5-FeO-MO$ ($M=Mg, Ca, Ba$); $\ast$, $P_2O_5-V_2O_5$; $\triangleright$, $P_2O_5-FeO$; $+$, $TeO_2-V_2O_5$.

The figure shows that dependence for the selected glasses that exhibit $s=0.70 \pm 0.03$ in the relation $\sigma_{ac}=A\omega^s$ measured by an ac bridge. From the slope we have obtained $s=0.70$ for $f=10$kHz as well as for $f=10$MHz.

The activation energy for ac conductivity $W_{ac}$ is related to $W_{dc}$ as:

$$W_{ac} = W_{dc} (1-s)$$
ELECTRICAL MODULUS

\[ M^* = M' + jM'' = \frac{\varepsilon'}{(\varepsilon')^2 + (\varepsilon'')^2} + j\frac{\varepsilon''}{(\varepsilon')^2 + (\varepsilon'')^2} \]

The imaginary part \( M''(\omega) \) always shows peaks, which positions depend on the value of dc conductivity. The activation energy of the peak is the same as those observed in dc conductivity.

*The imaginary part of electrical modulus \( M'' \) versus frequency in iron-phosphate glass.*

depend on the value of dc conductivity. The activation energy of the peak is the same as those observed in dc conductivity.
The imaginary \( M'' \) versus real \( M' \) part of electrical modulus in iron-borate glass for different temperatures: 296 K, 325 K, 348 K, 369 K, 402 K, 453K

Two regions are well distinguished in the complex plot of electric modulus \( M^* \) where all data points for different temperatures are resided on the single plot. Below \( M''_{\text{max}} \) dominates dc conductivity and all the data points are laying on the arc of semicircle. A different feature is observed for high frequencies, above \( M''_{\text{max}} \) where ac conductivity prevails and follows the Jonscher power law. In this region all points are laying on a straight line. Taking into account Kramers-Kronig relation the corresponding expression for this region is:

\[
\frac{|M' - M'_{\infty}|}{M''} = \frac{(\varepsilon' - \varepsilon_{\infty})}{\varepsilon''} = \tan\frac{s\pi}{2}
\]

where \( s \) is the exponent in the Jonscher power law: \( F_{\text{ac}} = A T^s \).

The value of \( s \) obtained from the slope of the high frequency part of \( M^* \) corresponds to the average \( s \) evaluated from \( F_{\text{ac}} \).
The shape of \( M^* \) plot can be well explained in the frame of the Hunt theory, especially the lack of dependence on temperature. We have pointed out that \( g'' \) obeyed Arrhenius relation with the same activation energy as the dc conductivity. According to Kramers-Kronig relation the same should be observed for \( g' \). Therefore, no temperature dependence on the complex plane \( M^* \) is observed.

\[ g'' \text{ and } g' = g - g_d \text{ as a function of frequency in iron-phosphate glass (} T=300\text{K}) \]
Universality of ac conduction in disordered solids

Scaling properties

The real part of normalized conductivity $\sigma(\omega)/\sigma_{dc}$ as a function of scaled frequency according to scaling analysis of Roling [Solid State Ionics 105(1998) 185] in 50P$_2$O$_5$-40FeO-10BaO glass.

It is almost always possible to scale measurements of the frequency dependent conductivity into one single “master” curve.

Different solids have quite similar master curves. In particular, ac electronic and ionic conduction cannot be distinguished.

The only common feature of the numerous different solids exhibiting this ac universality is their disorder.
ELECTRONIC - IONIC CONDUCTIVITY IN TMO GLASSES CONTAINING ALKALI IONS (Li⁺, Na⁺, K⁺, Cs⁺) or Ag⁺, Cu⁺

We can distinguish two class of glasses:
I. TMO is a glass former:
   V₂O₅, WO₃, MoO₃

*Typical glasses:*
   - P₂O₅-V₂O₅-A₂O
   - P₂O₅-WO₃-A₂O
   - P₂O₅-MoO₃-A₂O
   - TeO₂-V₂O₅-A₂O
   where A is an alkali ion

*Properties:*
Conductivity anomalies are observed. Deep minima in conductivity occur when some amounts of A₂O are introduced into the glass network.

*Examples:*

\[
P₂O₅ - WO₃ - Li₂O
\]

\[P₂O₅ = \text{const} \quad 40 \text{ mol}\%\]

\[WO₃ = \text{const} \quad 55 \text{ mol}\%\]

60V$_2$O$_5$-(40-x)P$_2$O$_5$-xR$_2$O glasses:
1 - Li$_2$O; 2 - Na$_2$O, 3 - K$_2$O, 4 - Rb$_2$O, 5 - Cs$_2$O, 6 - Ag$_2$O, 7 - Tl$_2$O

**Interpretations:**

1. Ion-polaron interaction
The mobile electrons (polarons) are attracted to oppositely charged A$^+$ ions and create cation-polaron pairs which move together as neutral entities.

2. Ionic path and electronic path are independent. Addition of A$_2$O (or replacement TMO by A$_2$O) causes the breaking of the electron percolation paths
II. TMO is a network modifier

1. Copper oxides: CuO, Cu$_2$O

*Typical glasses:*

- P$_2$O$_5$ - CuO;  P$_2$O$_5$ -MO-CuO, (M=Ba, Ca)
- Bi-Sr-Ca-Cu-O (glass precursor for high Tc superconducting ceramics)
- TeO$_2$-CuO,  TeO$_2$-MO-CuO (M=Ba,Ca)
- B$_2$O$_3$-CuO,  B$_2$O$_3$-MO-CuO (M=Ba,Ca)

*Properties:*

Electronic conductivity: *electron hopping between Cu$^+$ to Cu$^{2+}$*

Ionic Conductivity: *Cu$^+$ ion is mobile in glass*

Cu$^+$ ions participate in electronic and ionic conduction.

Conductivity increases with increasing ratio: Cu$^+$/ (Cu$^+$+Cu$^{2+}$)

*Examples*

![Graph showing conductivity vs. ratio](image)

2. Iron oxides: \( \text{FeO, Fe}_2\text{O}_3 \)

Typical glasses:
\[
P_2\text{O}_5 - \text{FeO-A}_2\text{O}; \quad P_2\text{O}_5 - \text{Fe}_2\text{O}_3-A_2\text{O}
\]

Properties:
1. The conductivity varies slightly in the glass with different alkali content.
2. The conductivity in alkali-iron-phosphate glasses \(< 20 \text{ mol}\%A_2\text{O} \) depends mainly upon iron oxide content which suggests electronic conduction.

Examples:

It is shown that the replacement of \( \text{CaO} \) by \( \text{Na}_2\text{O} \) caused rather small increase in ac conductivity.

The alkali ions have smaller mobility and are bonded to the \( \text{Fe-O-P} \) network.
The conduction in these glasses is predominantly electronic controlled by electron hopping between Fe(II) and Fe(III) sites.

A similar behaviour is observed in P$_2$O$_5$-Fe$_2$O$_3$-Cs$_2$O glasses
INTERNAL FRICTION

The fundamental measure of internal friction $Q^{-1}$ is the ratio $\Delta W/W$, where $W$ is the vibrational energy and $\Delta W$ is the energy dissipated during one oscillation period.

Usually the internal friction $Q^{-1}$ is determined by the measurements of logarithmic decrement of damping of free vibration $\delta$.

If the internal friction is small and does not depend on the amplitude of vibrations one can obtain simple relations between parameters describing mechanical energy losses:

$$Q^{-1} = \frac{\Delta W}{2\pi W} = \frac{\delta}{\pi}$$

Measurements of the internal friction of fibres 20 to 50 mm in length were performed with torsium pendulum at 0.2 to 20 Hz while heating the fibers at 1 K/min from 120 to 700 K. The vibration frequency, $f$, was recorded since the shear modulus, $G$, is proportional to $f^2$. The internal friction ($Q^{-1}$) can be determined from the free torsional vibrations using the following formula:

$$Q^{-1} = \frac{1}{n\pi} \ln\left(\frac{A_0}{A_n}\right)$$

where $n$ represents the number of vibrations and $A_0$ and $A_n$ are the amplitudes of the first and nth vibrations, respectively.
Internal friction in electronic conducting glasses

Internal friction in iron-phosphate glass. Peak 1 is related to the iron ions contents. The activation energy of this peak is the same as that for dc conductivity: $W_{dc} = W_{IF} = 0.63$ eV

Internal friction in $\text{P}_2\text{O}_5$-$\text{MgO}$ glass. The low temperature peak is disappeared in glass without iron oxide.
Internal friction in electronic-ionic conducting glasses

Example: $P_2O_5-V_2O_5-Na_2O$ glass

The internal friction spectra revealed two peaks 1 and 2' that are attributed to the electronic hopping and alkali ions migration respectively. For glasses containing up to 25 mol% Na$_2$O we may precisely characterize the process of electron (peak1) and sodium (peak 2) migration including their activation energies. Such complete characteristics is rather difficult to obtain by impedance spectroscopy.

A comparison of internal friction and impedance spectroscopy indicate that the internal friction is a more sensitive method for detecting the movement of ions in the glass network.