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# Optical absorption of ion-conducting glasses as transformed from ac data

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For a condensed medium, optical data and electrical data can be transformed to each other. A general procedure for calculating an optical absorption coefficient from ac data was given. Tests were made for two ion conducting glasses using ac data near the frequencies of relaxation for conduction, above the frequencies of which the ionic conductivities are expected to decrease. © *2001 Kluwer Academic Publishers*

## 1. Introduction

In the optical measurement of a condensed medium, in the frequency range of $>10^7$ Hz, a sample is irradiated with light of intensity $I_0$ and the transmitted light of intensity $I$ is measured as a function of frequency, to obtain the optical absorption coefficient, $\eta$, from

$$I = I_0 \exp(-\eta d), \tag{1}$$

where $d$ is a sample thickness.

On the other hand, in the ac electric measurement in the frequency range of $<10^7$ Hz, we deposit metal electrodes on both sides of a sample, bias it with an ac electric field

$$E^* = E_0 \exp[-j(\omega t - Kr)], \tag{2}$$

and observe the induced current in the external circuit. The induced current is usually represented by the admittance, $Y^*$, which is given by

$$Y^* = I_p^* \big/ V_p = G + jB, \tag{3}$$

where $I_p^*$ is the (complex) peak current, $V_p(=E_0 d)$ is the peak voltage, $G$ is the conductance, and $B$ is the susceptance.

When we use an ac technique for studying ion dynamics in ion-conducting glass, we are apt to think that what we are seeing is an electrical response of a sample and not an optical one. Of course, because of large difference in relevant frequency windows, both techniques survey different phenomena in general. Yet, the electrical response can be transformed into the optical response and vice versa, because both arise from interactions of the electromagnetic wave with a sample. As a result, the response of a sample over very wide frequencies can be represented either in the whole electrical or in the whole optical spectrum.

The purpose of the present work is to evaluate $\eta$ for two ion-conducting glasses as examples using ac electric data obtained near the frequencies of relaxation of mobile ions for conduction. A general procedure for evaluating $\eta$ from the ac data is given first.

## 2. Theoretical

The interaction between an electromagnetic wave and a material is described by the Maxwell's equations, like

$$rot H^* = \sigma^* E^* + \varepsilon_0 \varepsilon^* \partial E^* \big/ \partial t, \tag{4}$$

where $H^*$ is the magnetic field, $\sigma^*(=\sigma_1 + j\sigma_2)$ is the conductivity, $\varepsilon^*(= \varepsilon_1 + j\varepsilon_2)$ is the dielectric function, and $\varepsilon_0$ is the permittivity of free space. From Equations 2 and 4 and others the propagation constant, $K$, is given by

$$\begin{aligned} K &= (\omega/c)\left(\varepsilon^* + j\sigma^*/\omega\varepsilon_0\right)^{1/2} \\ &= (\omega/c)N^*, \end{aligned} \tag{5}$$

which shows that the velocity of the electromagnetic wave is reduced from $c$ to $c/N^*(N^*(=n+jk)$ being the refractive index, where $n$ and $k$ are the optical constants) when the wave travels through a material.

As Equation 4 suggests, the charge carrier motion in a condensed medium can be classified into conduction ($\longleftrightarrow\sigma^*$) and polarization ($\longleftrightarrow\varepsilon^*$). Here, conduction refers to the motion of free charge carriers while polarization refers to the motion of bound charge carriers. At frequencies of $<10^7$ Hz at which light of strong-enough intensity and a good detector are not available, we must deposit metal electrodes on both sides of a sample and extract conduction by electron transfer and polarization by electron accumulation/depletion via the sample-electrode interfaces. For a sample of the thickness $d$ and the electrode area $s$, the response can be given by

$$rot H^* = (d/s)Y^* E^*. \tag{6}$$

From Equations 4 and 6, we obtain the relations

$$(d/s)G = \sigma_1 + \varepsilon_0\varepsilon_2\omega \tag{7}$$

and

$$(d/s)B = \sigma_2 - \varepsilon_0\varepsilon_1\omega. \tag{8}$$

Then,

$$\begin{aligned} N^{*2} &= (1/\omega\varepsilon_0)[-(\sigma_2 - \varepsilon_0\varepsilon_1\omega) + j(\sigma_1 + \varepsilon_0\varepsilon_2\omega)] \\ &= (d/s\omega\varepsilon_0)(-B + jG) = jdY^*/s\omega\varepsilon_0. \end{aligned} \tag{9}$$

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Let us define the response function $\Sigma^*$ by

$$N^{*2} = \Sigma^* = \Sigma_1 + j\Sigma_2, \tag{10}$$

where

$$\Sigma_1 = -dB/s\omega\varepsilon_0 = \varepsilon_1 - \sigma_2/\omega\varepsilon_0 = n^2 - k^2 \tag{11}$$

and

$$\Sigma_2 = dG/s\omega\varepsilon_0 = \varepsilon_2 + \sigma_1/\omega\varepsilon_0 = 2nk. \tag{12}$$

What we observe experimentally is $\Sigma^*$ or $Y^*$, not $\sigma^*$ nor $\varepsilon^*$. They should not be confused. However, because of the difficulty in separating the conduction and polarization parts, their sum is usually represented again by $\sigma^*$ or $\varepsilon^*$.

When an electromagnetic wave travels through a material, it would decay. The absorption coefficient, $\eta$, which characterizes decay is given by

$$\eta = 2\omega k/c. \tag{13}$$

From Equations 5–9,

$$\begin{aligned}\eta &= (2\omega/c)\left[\left\{\left(\Sigma_1^2 + \Sigma_2^2\right)^{1/2} - \Sigma_1\right\}/2\right]^{1/2}\\ &= (1/c)\left[2d\omega(/Y^*/+B)/s\varepsilon_0\right]^{1/2}.\end{aligned} \tag{14}$$

In an ion-conducting glass, the elementary process of conduction (governed by the ionic relaxation time $\tau$) accompanies polarization in one-to-one correspondence, to yield the universal relation [3–5]

$$\sigma_{dc} = \varepsilon_0\Delta\varepsilon/\tau = 2\pi f_r\varepsilon_0\Delta\varepsilon \tag{15}$$

between the dc conductivity, $\sigma_{dc}$, and the amount of dielectric dispersion, $\Delta\varepsilon$, where $f_r$ is the frequency of relaxation for conduction which satisfies

$$\omega_r\tau = 2\pi f_r\tau = 1. \tag{16}$$

This conduction-related polarization satisfies the Debye equation

$$\varepsilon^* = \varepsilon_\infty + \Delta\varepsilon/(1 - j\omega\tau), \tag{17}$$

although it is believed by many workers that $\tau$ has distribution due to the disordered structure of glass.

The charge density which flows to a particular electrode at an extremely high frequency is

$$Q^*_\infty = \varepsilon_0\varepsilon_\infty E^*, \tag{18}$$

while the charge density at a given frequency is

$$Q^* = \varepsilon_0\varepsilon^* E^*. \tag{19}$$

By one-to-one correspondence between ionic conduction and conduction-related polarization, the relation (the real part of which gives Equation 15)

$$\Delta Q^*/\tau E^* = \left(Q^* - Q^*_\infty\right)/\tau E^* = \varepsilon_0\left(\varepsilon^* - \varepsilon_\infty\right)/\tau = \sigma^* \tag{20}$$

should hold. From Equations 15, 17, and 20, one obtains the Drude equation

$$\sigma^* = \sigma_{dc}/(1 - j\omega\tau) \tag{21}$$

which originally was derived for free-electron metal. This identity in form of the frequency dependences of electronic and ionic conductivities means that, irrespective of the charge carriers involved, the conductivity should decrease with increasing frequencies above $f_r$ by increasing difficulties of the charge carriers to follow changes of the polarity of the electromagnetic wave.

As is suggested from Equation 14, $\eta$ has contributions from conduction and polarization. Provided conduction is the sole contributor, $\eta$ is expected from Equation 21 to approach the critical value

$$\eta_c = (2/c)(\sigma_{dc}/\varepsilon_0\tau)^{1/2} \tag{22}$$

when $\omega \gg 1/\tau$.

The aim of the present work was to evaluate $\eta$ from ac data of the $Na_2O$–$B_2O_3$ (abbreviated as N2B) glass at 23°C [1] and the 75AgI-25$Ag_4P_2O_7$ (abbreviated as AgI) glass at −147°C [2], both near the respective frequencies of relaxation for conduction. They were chosen as a typical ion-conducting glass and superion-conducting glass, respectively.

## 3. Results and discussion

Figs 1 and 2 show the $\eta$ curves for both glasses, as evaluated from Equation 14 using the observed $G$ and $B$ (Figs 3 and 4). Also shown in the figures are the

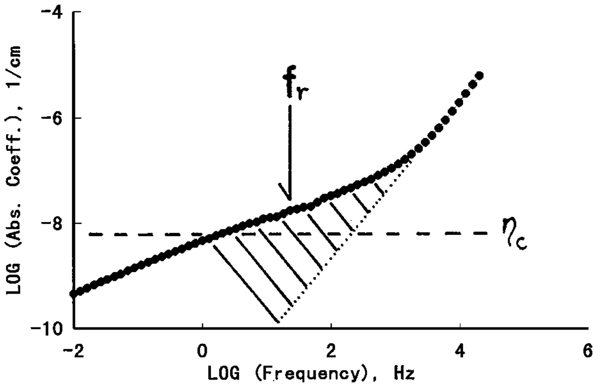

*Figure 1* Optical absorption coefficient, $\eta$, of N2B glass near $\omega \sim 1/\tau$ at 23°C. Also shown are $f_r$ and $\eta_c$ estimated using $1.47 \times 10^{-10}$ S cm$^{-1}$ for $\sigma_{dc}$ and 12 for $\Delta\varepsilon$. The shaded region is ascribed to be the contribution to $\eta$ from ionic conduction.

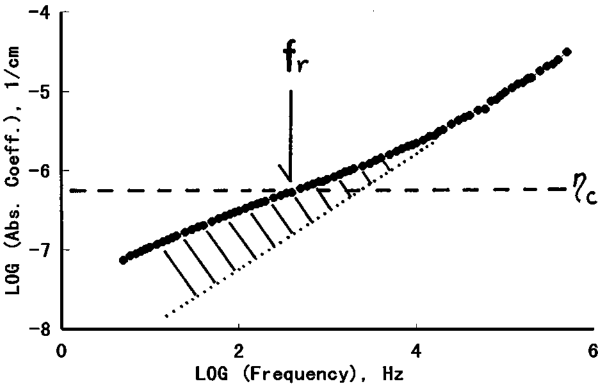

*Figure 2* Optical absorption coefficient, $\eta$, of AgI glass near $\omega \sim 1/\tau$ at −147°C. Also shown are $f_r$ and $\eta_c$ estimated using $7.54 \times 10^{-9}$ S cm$^{-1}$ for $\sigma_{dc}$ and 35 for $\Delta\varepsilon$. The shaded region is ascribed to be the contribution to $\eta$ from ionic conduction.

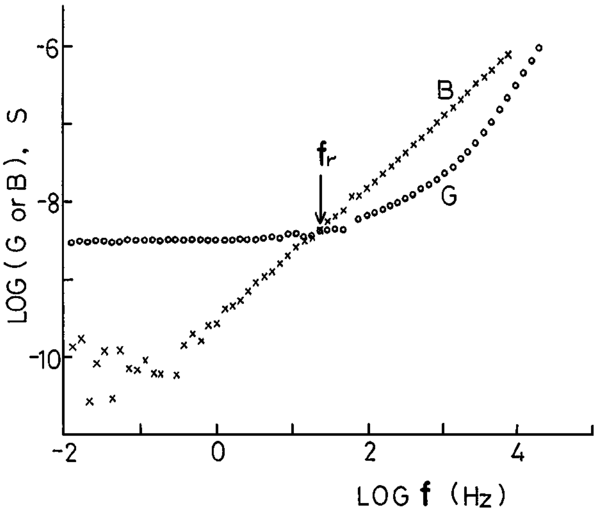

*Figure 3* Frequency dependences of $G$ and $B$ for N2B glass at 23°C [1], as well as the frequency of relaxation for conduction, $f_r$, at which $\omega_r = 1/\tau$.

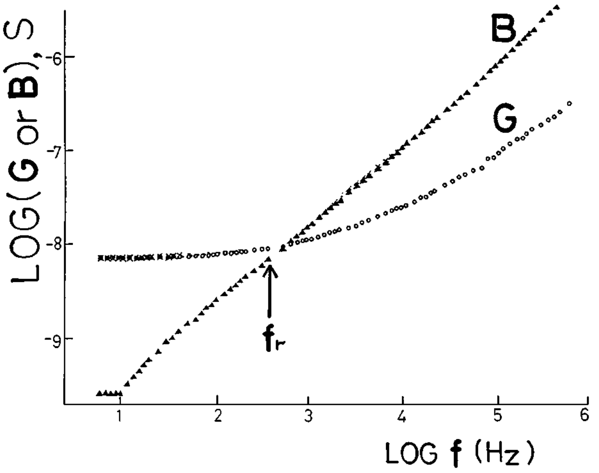

*Figure 4* Frequency dependences of $G$ and $B$ for AgI glass at −147°C [2], as well as the frequency of relaxation for conduction, $f_r$, at which $\omega_r = 1/\tau$.

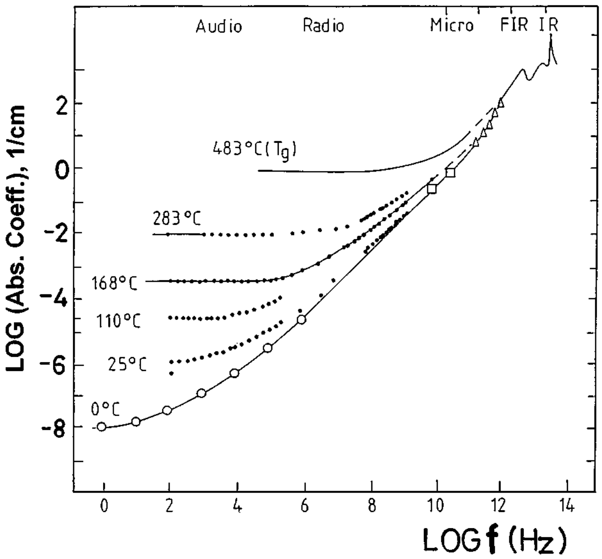

*Figure 5* Optical absorption coefficient of $Na_2O$-$3SiO_2$ glass over wide frequency range up to the infra-red [7].

$\eta_c$ and $f_r$ values evaluated from Equation 22 and 15, respectively, using the reported values of $\sigma_{dc}$ and $\Delta\varepsilon$. For N2B glass, the relaxation of sodium ions was studied in the frequency-, temperature-, and time-domains from which $\Delta\varepsilon$ was estimated to be around 12 at 23°C [1]. Similarly, $\Delta\varepsilon$ for the relaxation of silver ions in AgI glass was estimated to be around 35 at −147°C [2].

In the frequency ranges measured, the electrical response of the samples is well described by parallel combination of the resistance, $R$, and the capacitance, $C$, of the bulk. The equivalent circuit of any single phase is a parallel $RC$, with $R(=1/G)$ and $C(=B/\omega)$ representing, respectively, the in-phase and 90° out-of-phase components of the response to ac bias voltage.

At lower frequencies than this, we encounter "electrode polarization" as a result of appearance of an additional phase (or phases) at the electrode-glass interface(s). Another parallel $RC$ circuit must be added in series to the bulky $RC$ circuit for representing the response [6]. There remains a question whether it is possible to transform the electrical response into the optical response when "electrode polarization" comes into play. The response is no more reproducible, nor of intrinsic origin but is electrode-related. Our data (Figs 3 and 4), on the other hand, were reproducible and of intrinsic origin.

Although $\eta$ increases with frequencies for both glasses, shows deflection more upward at some frequency above $f_r$. Contrary to a crystalline material, glass is believed to have a distribution in $\tau$. As a result, the $\varepsilon_1$ dispersion/$\varepsilon_2$ absorption are broadened from the Debye's description (Equation 17) and that $\varepsilon_1$ and $\varepsilon_2$ decrease slowly over more than four decades of frequencies above $f_r$ [2]. It is suggested, then, that the slowly decreasing $\varepsilon^*$ would become dominant at frequencies above $f_r$, and enhance $\eta$. The shaded regions in Figs 1 and 2, on the other hand, are expected to be by the contribution from the conduction term. The convergences of $f_r$ and $\eta_c$ to the uppermost portion of the shade support our assignment. According to Equations 16 and 21, conduction would cease contributing at some frequency above $f_r$, even if we accept large distribution in $\tau$. The difference in $\sigma_{dc}$, $\sigma_{dc}(\text{AgI})/\sigma_{dc}(\text{N2B}) \sim 50$, reflects the difference in $\eta_c$ for the two glasses. That is, the higher the dc conductivity, the higher would be the optical absorption coefficient.

From Equations 12 and 13 one obtains the relation

$$\eta = \sigma_{ac}/nc\varepsilon_0 \tag{23}$$

provided the ac conductivity, $\sigma_{ac}$, is defined (as many workers do) by

$$\sigma_{ac} = dG/s. \tag{24}$$

Wong and Angell [7] joined the infrared data and the ac data of the $Na_2O$–$3SiO_2$ glass, in the frequency range of $10^{\circ}$ to $10^{14}$ Hz, by Equation 23 (Fig. 5). Their $\eta$ curves, however, give plateaus at frequencies near $f_r$ in parallel with $G$ plateaus due to ionic conduction (Figs 3 and 4). This disagrees with ours (Figs 1 and 2). This inconsistency arises from their assumption that $n(\omega)$ is constant (1.9 for the $Na_2O$-$3SiO_2$ glass) over wide

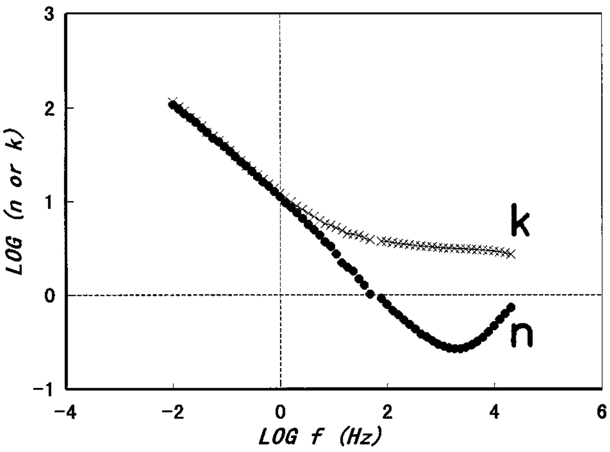

*Figure 6* Optical constants ($n$ and $k$) of N2B glass near $\omega \sim 1/\tau$ at 23 °C.

frequency range. The truth is that $n(\omega)$ is not at all constant near $f_r$, as is evident by frequency dependences of the optical constants for our N2B glass (Fig. 6).

## 4. Conclusions

Optical data and electrical data can be transformed to each other. That is, to put the electrodes on both sides of a sample, bias it with ac voltage and measure the electrical response is equivalent to measuring optical absorption of the sample in the corresponding frequency range. A general procedure for calculating an optical absorption coefficient from ac data was given.

The optical absorption coefficients, $\eta$, were calculated for two ion-conducting glasses using the ac electric data near the frequencies of relaxation for conduction, $f_r$. At frequencies below $f_r$, $\eta$ is dominated by the conduction term. At frequencies near $f_r$, the conduction-dominated $\eta$ coincides well with $\eta_c$ estimated. Finally, at frequencies above $f_r$, the contribution from ionic conduction decreases and is gradually overwhelmed by the growing contribution from the polarization term, by which the $\eta$ curve is deflected more upward at some point above $f_r$.

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