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A method of determination of electrical conduction mechanisms in complex amorphous materials

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ABSTRACT

A novel approach to determine conduction mechanisms in complex amorphous materials was presented and tested on a real system. In the first step of the presented method, total electrical admittance of the material is analyzed in order to separate a couple of processes, each of which can be described by Jonscher's universal dielectric response. In the following step, a temperature dependence of dielectric response parameters of the processes is determined and compared with known models of conduction mechanisms in structural amorphous materials. Using this approach, a presence of two different conduction mechanisms describing electrical conductivity in a two-phase glass was described.

1. Introduction

The characteristic property of dielectric materials is a strong dispersion of the ac conductance (Y'). At low frequencies, one observes a frequency-independent dc conductance (Y_{dc}), while at higher frequencies conductance usually varies as a power of the frequency, what overall may be written as Eq. (1):

$$Y'(\omega) = Y_{dc} + A\omega^n, \tag{1}$$

where $\omega = 2\pi f$ is an angular frequency, and parameters A and n can be temperature dependent. The increase in conductance usually continues up to phonon frequency ($\omega_{ph} \approx 10^{12}\, s^{-1}$) [1].

In a series of publications, Jonsher [1–4] proposed and demonstrated the utility of Eq. (1) in order to analyze the ac conductivity in amorphous systems. This relation found application in almost every disorder solid and therefore it was named as a *universal dielectric response* (UDR). Further, it has been found [4] that UDR (Eq. (1)) may be written in a full complex form in terms of admittance (Y^*) as:

$$Y^*(\omega) = Y_0\left[1 + (j\omega\tau)^n\right] = Y_0\left[(\omega\tau)^n\left(cos\left(n\frac{\pi}{2}\right) + jsin\left(n\frac{\pi}{2}\right)\right)\right], \tag{2}$$

where j is an imaginary unit, τ is a relaxation time of a conduction process and exponent parameter n is less than one. The relaxation time τ is often replaced by a frequency ($\omega_0 = \tau^{-1}$) of charge carrier hopping between active sites. As can be seen, Eq. (1) is exactly a real part of Eq. (2).

Much effort was done to create theoretical models, which explain the frequency and temperature dependencies of electrical properties. The most used models [5, 6] are based on an assumption that a charge carrier moves between localized sites separated by finite distances and energy barrier potentials. There are several popular models of electrical charge transport, which describe the conductivity behavior of amorphous materials: small polaron hopping (SPH) [8], overlapping large polaron hopping (OLPH) [9, 10], correlated barrier hopping (CBH) [11], quantum mechanical tunneling (QMT) [9] and continuous time random walk (CTRW) [12, 13]. For all mentioned models, Elliott [6] calculated that exponential factor n in UDR equation (Eq. (1)) should vary in a different fashion with temperature. According to Elliott's calculations [6], parameter n for QMT and CTWR models should be temperature independent, while with an increase in temperature it should decrease for CBH or increase for SPH. Only for OLPH exponential factor n may increase or decrease with increase in temperature, and the direction of changes depends on conduction process parameters like polaron radius, activation energy and decay of electron wave function. Since in many materials [5–7] the exponential factor n, obtained by fitting admittance to Eq. (2), is temperature dependent, it is possible to determine conduction process mechanisms by comparing experimentally obtained $n = f(T)$ function with theoretical models [14].

Usually, to determine electrical properties of different relaxation processes, the conductance of the system is modeled by equivalent electrical circuits composed of discrete components like resistors, capacitors, constant phase elements (*CPE*) or Warburg's elements. Although these elements can be arranged in many different

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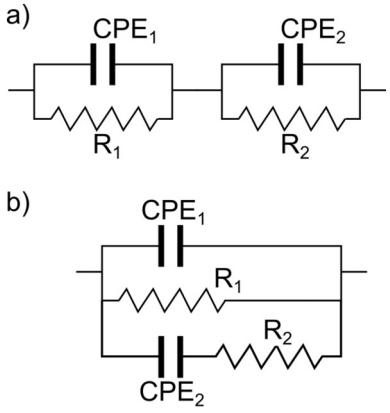

Fig. 1. Scheme of simulated electrical circuits with two relaxation times a) Voigt and b) Maxwell networks.

configurations, two of them are commonly used i.e., Voigt and Maxwell networks (Fig. 1a and Fig. 1b respectively) [7]. Depending on the configuration, different information about the same analyzed system can be evaluated. For instance in Voigt network, each of R_i and CPE_i elements in the circuit can be related to certain resistance and capacitance of conducting region. In Maxwell network, the global R_1 and CPE_1 parameters may be related to resistance and capacitance of process extended to the whole system, while R_i and CPE_i (for $i > 1$) refer only to the resistance and capacitance of electrical conduction process which is blocked.

A simple Voigt circuit characterized by a presence of two relaxation processes and built of two resistors and two *CPEs* is shown in Fig. 1a. As admittance of *CPE* is described by Eq. (3):

$$Y^*_{CPE}(\omega) = A(j\omega\tau)^n = A(\omega\tau)^n\left(cos\left(n\frac{\pi}{2}\right) + jsin\left(n\frac{\pi}{2}\right)\right), \tag{3}$$

then total admittance of a single $R - CPE$ sub-circuit is defined by Eq. (4):

$$\begin{aligned} Y^*(\omega) &= Y_R + Y^*_{CPE} = \frac{1}{R} + A(j\omega\tau)^n \\ &= \frac{1}{R} + A(\omega\tau)^n\left(cos\left(n\frac{\pi}{2}\right) + jsin\left(n\frac{\pi}{2}\right)\right), \end{aligned} \tag{4}$$

The admittance described by Jonscher's UDR equation (Eq. (2)) and of a simple $R - CPE$ circuit (Eq. (4)) is mathematically equivalent what has been shown by Macdonald [7]. In a consequence, the admittance of the whole Voigt circuit shown in Fig. 1a can be described by Eq. (5):

$$Y^* = \frac{Y^*_1 Y^*_2}{Y^*_1 + Y^*_2} = \frac{(1 + R_1A_1(j\omega\tau_1)^{n_1})(1 + R_2A_2(j\omega\tau_2)^{n_2})}{R_1(1 + R_2A_2(j\omega\tau_2)^{n_2}) + R_2(1 + R_1A_1(j\omega\tau_1)^{n_1})}, \tag{5}$$

while the admittance of equivalent Maxwell circuit (Fig. 1b) may be expressed by Eq. (6):

$$Y^* = Y^*_1 + Y^*_2 = \frac{1}{R_1} + A_1(j\omega\tau_1)^{n_1} + \frac{A_2(j\omega\tau_2)^{n_2}}{1 + R_2A_2(j\omega\tau_2)^{n_2}}, \tag{6}$$

where n_1 and n_2 are constants, τ_1 and τ_2 define a characteristic time of a relaxation processes, while $A_1R_1(j\omega\tau)^{n1}$ and $A_2R_2(j\omega\tau)^{n2}$*have* unit equal to 1.

One of the example of disordered materials, which exhibit two relaxation processes in their conductivity curves, is double-phase glasses. An interpretation of its electrical properties is especially interesting when it is produced without an addition of alkali metal ions because the most possible mechanism of charge movement in both phases is polaron hopping exhibiting different physical properties [5]. In the present article, the method of conduction mechanisms analysis is presented for any system characterized by two relaxation processes of charge transport. Next, this method was applied to a real glass system 50MnO – $30SiO_2$ – $20B_2O_3$ (in mol%) not containing alkali ions and exhibiting uniform phases separation. Finally, models accurately describing the conductivity of founded processes were determined.

2. Experimental

The glass of a composition of 50MnO - $30SiO_2$ - $20B_2O_3$, was prepared using appropriate amounts of analytical grade: MnO_2 (Sigma-Aldrich), SiO_2 (POCH), and H_3BO_3 (POCH) powders. The stoichiometric composition of reagents was mixed manually in an agate mortar and heated up in a muffle furnace in a platinum crucible. The mixture was melted at 1500 K for 30 min in air. The melt was quenched by pouring on a preheated to about 500 K brass plate and pressing by another plate to obtain flat circular pellets of 1–1.3 mm thickness and 10–20 mm in the diameter. In order to study properties related to the bulk material, before measurements, a surface layer was removed from pellets by grinding with a dry sandpaper. Powder X-ray diffraction (XRD) measurement was done at room temperature on PANalytical X'Pert Pro MPD using the CuK_α radiation in order to check the glass structure. The microstructure of the sample was investigated with FEI Quanta 250 FEG Scanning Electron Microscope (SEM). Before measurement, glass sample was covered by a 20 nm gold layer with a vacuum sputtering equipment.

Electrical properties were examined by impedance spectroscopy measurements, which were carried out in the temperature range of 445 K - 760 K with the Novocontrol Concept 40 broadband dielectric spectrometer. The used frequency range was from 10 mHz to 1 MHz and the ac signal was 1 V_{rms}. Before measurements, the pellet of glass was polished to obtain plane parallel samples. Circular gold electrodes of 9–12 mm in the diameter were deposited by vacuum sputtering on sample basal surfaces. The measurement error of electrical properties was minimalized by calibration impedance spectrometer by a calibration procedure using 100 Ω resistors. On the other hand, random errors were minimalized by performed measurement for every point at least 3 times.

3. Method

An analysis of possible mechanisms of charge carrier movement in the glass, characterized by two relaxation processes, was performed. It was done based on a frequency and temperature behavior of admittance. The analysis of admittance parameters consisted of few steps. In the first step, an equivalent electrical circuit (combined of resistors and CPEs) is proposed, which represents as many relaxation processes as are observed in a measured system. In the second step, the equation describing admittance of the equivalent circuit is used for fitting the measured data. Depending on the interesting properties of the system, equations describing Voigt (Eq. (5)) or Maxwell (Eq. (6)) networks can be fitted to the admittance data. For instance, using Voigt network to analyze two phases, material R_1 and R_2 are resistances of these phases, while τ_1 and τ_2 – their relaxation time. It can be seen, that four parameters (i.e., A_i, R_i, τ_i, and n_i) correspond with each relaxation process. The fitting procedure is performed simultaneously on the real and the imaginary part of admittance using least-squares methods (Levenberg-Marquardt algorithm [15]). Next, obtained parameters (especially n factors) are analyzed as a function of temperature. Finally, the relations describing different conduction mechanism models are fitted to $n_i = f(T)$ function and obtained parameters are compared with the real values. All measurement data were analyzed and fitted using OrignPro9.1 software with implemented complex numbers library. Standard errors for the derived parameters were estimated according to the error propagation formula, which in OroginPro9.1 is an approximate formula [16].