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On the origin of electrical relaxation in tellurite glasses

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ABSTRACT

The dielectric properties of ternary silver vanadium tellurite and titanium vanadium tellurite glasses of the form [0.5[xAg$_2$O-(1 − x)V$_2$O$_5$]–0.5TeO$_2$, x = 0.1–0.8 mol] and [0.5[xTiO$_2$-(1 − x)V$_2$O$_5$]–0.5TeO$_2$, x = 0.1–0.6 mol] are investigated as a function of frequency (10 Hz–1 MHz) and temperature (70–425 K). Electrical relaxation is analyzed in terms of dielectric modulus and Kohlrausch–Williams–Watts (KWW) stretched exponential distribution function. The composition dependence of the stretched exponential parameter (β) is explained according to the variation of activation energy for dc conductivity and inter-charge separation in the two glass series. From the transition of polaronic to ionic conduction in silver vanadium tellurite glass series, it is established that ion–ion correlations are more effective in slowing down the electrical relaxation than the interactions between electronic charge carriers.

1. Introduction

Charge transport studies in mixed ionic-semiconducting glasses have become a topic of current research mainly due to their potential applications in solid state devices. Oxide glasses containing transition metal ions (TMI), such as V, Fe, Cu, etc., are of great interest because they exhibit semiconducting properties due to the existence of transition metal ions in two different states. In V$_2$O$_5$ containing glasses conduction occurs by hopping of small polarons from low valance state V^{4+} to high valance state V^{5+}. On adding BaO, the electronic paths get progressively blocked, causing a decrease in electronic conductivity [1]. Here Ba ion acts as glass modifier, creates non-bridging oxygen (NBO) and breaks the glass network. Among the various types of oxide glasses, the tellurite based glasses exhibit relatively high dielectric constant and electrical conductivity, which has been argued as due to the unshared pair of electrons of the TeO$_4$ group that take part in bonding [2]. Ac and dc conductivity (σ), and dielectric constant (ε) of tellurite glasses doped with transition metal oxide such as of tungsten, molybdenum or vanadium have been reported in many articles [3–11]. Theoretical description of electrical conduction has been obtained for binary tungsten tellurite glasses based on the data over a wide range of temperature and electron–phonon coupling [6]. For the case of (TeO$_2$)$_{0.95}$(CeO$_2$)$_{0.05}$ glasses it is shown from the temperature dependence of conductivity and electron spin resonance that the carriers become localized at low temperature, but at high temperature the conductivity arises from the hopping of carriers between cerium sites [8].

The frequency and temperature dependence of the dielectric constant of binary tungsten tellurite and molybdenum tellurite glasses have been measured, and correlated with composition according to the value of the polarizability and the number of polarizable atoms per unit volume, which depend on the type and percentage of the modifier ions [4,9]. The dielectric relaxation in V$_2$O$_5$–TeO$_2$, CoO–V$_2$O$_5$–TeO$_2$ [12], ZnF$_2$–As$_2$O$_3$–V$_2$O$_5$–TeO$_2$ [13], and BaO–V$_2$O$_5$–TeO$_2$ [14] transition metal tellurite glasses has been reported recently. These published works indicate that the structural disorder in the network increases with the concentration of V$_2$O$_5$. The data also show an increase in dielectric constant as well as loss tangent, reflecting an increase in the concentration of V^{4+} ions that take part in charge transport and modify the glass network.

In a previous work on vanadium tellurite and silver vanadium tellurite glass systems [10,11] we established the role of V$_2$O$_5$ and Ag$_2$O on the complex structural change and how it affects the dc conduction mechanism. The experimental data for ac conductivity indicated that the conduction mechanism changes from being predominantly electronic to ionic at Ag$_2$O content >27.5 mol% [10]. The dc conductivity of the same silver vanadium tellurite glass systems resulted from non-adiabatic small polaron hopping of electrons [11]. Our objective in this article is to use this knowledge of conductivity to understand how the electrical relaxation process is affected by the transition from electronic to ionic conduction as V$_2$O$_5$ is replaced by Ag$_2$O mol%. We utilize modulus formalism to assess the electrical relaxation process.

2. Experimental work

The silver vanadium tellurite and titanium vanadium tellurite glass samples [0.5[xAg$_2$O-(1 − x)V$_2$O$_5$]–0.5TeO$_2$, x = 0.1–0.8], or [0.5[xTiO$_2$-(1 −

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x)V_2O_5]–0.5TeO_2, x = 0.1–0.6] were prepared by the standard melt-quenching technique, using high purity TeO_2 (99.99%), Ag_2O (99.99%), and reagent grade V_2O_5 (99.6%) (Aldrich Chemical Co., PA — USA). The annealed samples, which did not show any stress when viewed with polarized light, were polished down to about 1 mm thickness for electrical measurements as described in Ref. [10]. The X-ray diffraction analysis showed no indication of crystallinity in the samples. Also the samples were completely transparent and there was no difference in color with varying x. These observations suggest that silver was always present in the ionic form, rather than as metallic precipitate.

For electrical measurements, the flat surfaces of the cut samples, with dimension ≈1 cm^2 × 1 mm, were polished (down to 600 grit lapping paper) and cleaned. Silver electrodes were either painted directly on the two major surfaces, or deposited by vacuum evaporation and then covered with silver paste in the two-electrode configuration. Ac conductance, G, and capacitance, C, of a sample were measured with a precision automated capacitance bridge (model CGA-83) in the frequency range of 10 Hz to 1 MHz within the temperature range of 70–425 K. The complex dielectric constant ε^* has been calculated using

$$\varepsilon^* = \varepsilon^{/} - j\varepsilon^{//} \tag{1}$$

with,

$$\varepsilon^{/} = \frac{C}{C_o},\ \varepsilon^{//} = \frac{G}{C_o\omega}$$

where ω, C_o, $\varepsilon^{/}$ and $\varepsilon^{//}$ are angular frequency, capacitance of equivalent free space, real part of dielectric constant (or relative permittivity) and imaginary part of dielectric constant (or dielectric loss). The complex electric modulus M^* is then calculated according to

$$M^* \equiv \frac{1}{\varepsilon^*} = \frac{\varepsilon^{/} + j\varepsilon^{//}}{\varepsilon^{/2} + \varepsilon^{//2}} = M^{/} + jM^{//}. \tag{2}$$

The real, $M^{/}$, and imaginary, $M^{//}$, parts of M^* are simply given by the following equations:

$$M^{/} = \frac{\varepsilon^{/}}{\varepsilon^{/2} + \varepsilon^{//2}} \tag{3}$$

$$M^{//} = \frac{\varepsilon^{//}}{\varepsilon^{/2} + \varepsilon^{//2}}. \tag{4}$$

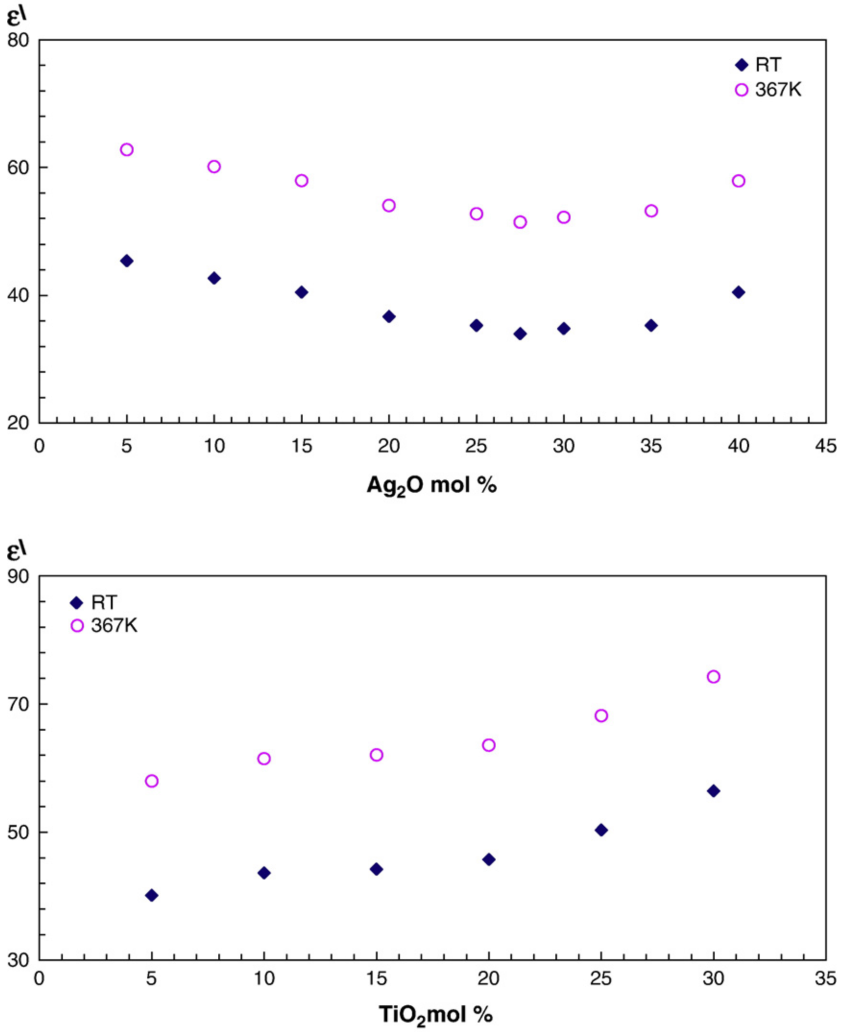

Fig. 1. The dielectric constant at 10^6 Hz and at two temperatures (RT and 367 K) for 0.5[xAg_2O-(1 − x)V_2O_5]–0.5TeO_2, and 0.5[xTiO_2-(1 − x)V_2O_5]–0.5TeO_2 glasses. Note that $\varepsilon^{\backslash}$ of pure TeO_2 glass and many binary tellurite glasses at 10^6 Hz and RT are 20.1 and 25–35, respectively (Refs. [4,9]).