Dielectric properties of vanadium phosphate glasses in a combined electric field

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The dielectric properties of vanadium phosphate glasses, composed of 70 mol % V_2O_5 and 30 mol % P_2O_5 with an addition of 1 wt % of CuO, have been measured under combined voltages simultaneously composed of dc voltages of 0, 30, 45 and 65 V, and an ac voltage of 0.5 V. Measurements were taken over a temperature range of 20–110 °C and a frequency range of $10–10^5$ Hz. The NiCr alloy electrodes used in this study were prepared by chemical vapour deposition techniques. The results of the measurements show that the conductivity and dielectric properties of the glasses could be described by a mechanism of electron hopping between energy states of the chain of molecules or by a tunneling effect. The transport of the electric charges involves movement across a potential barrier and the movement could be improved if the barrier was deformed by the dc voltage.

1. Introduction

The dielectric relaxation phenomena of vanadium phosphate glasses have been investigated by several authors [1–5]. However, these investigations were performed using either dc or ac voltages.

In this paper, we report the properties of these glasses and their behaviour in combined electrical fields when both dc and ac voltages are applied simultaneously. Measurements under such conditions are interesting, because many electrical systems and their components work under combined voltage conditions. Also, such studies can be useful not only from the practical point of view, but also in providing additional tests on the validity of existing theories of dielectric polarization.

The results of many authors obtained using single voltage conditions indicate that for defined temperature and frequency ranges electron relaxation polarization is predominant. In such a case the dielectric behaviour of a sample can be described by the Debye equations [6, 7] or by their modified version, the Cole–Cole equations [8].

The dielectric properties of the samples under consideration measured with different electrode materials also indicate the occurrence of a barrier layer at the surface of some electrodes [9]. The presence of such a layer implies interlayer migration polarization which can influence the complex electrical conductivity of the dielectric structure.

The aim of this paper is to present some experimental results and, on the basis of them to clarify the dielectric relaxation processes in the considered vanadium phosphate glasses.

2. The dielectric mechanism

A quantitative model of relaxation polarizations in the glasses under consideration is based on the idea of a potential barrier (Fig. 1a). If both dc and ac voltages are applied simultaneously, the potential barrier becomes asymmetric (Fig. 1b) and the probability of the transfer of charge carriers through the barrier becomes dependent on the direction of their motion. Usually, relaxation polarization processes are described by the Debye or Cole–Cole equations which consider a distribution of relaxation times on elementary relaxations. If fast and if both relaxation polarizations and dc conductivity are taken into consideration, the relative complex permittivity (ε^*) can be expressed [7] as follows:

$$\varepsilon^* = \varepsilon' - j\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (j\omega\tau_0)^{1-\alpha}} - j\frac{\sigma}{\omega\varepsilon_0} \quad (1)$$

where ε' is the relative permittivity (real part of ε^*), ε'' the loss permittivity (imaginary part of ε^*), j the imaginary unit, ε_∞ the relative permittivity for optical frequencies, ε_s the static relative permittivity, ω the angular frequency, τ_0 the most probable time of relaxation, α the distribution parameter, σ the dc conductivity of material and ε_0 the permittivity of a vacuum.

The relative complex permittivity, ε^*, consists of the real, ε', and imaginary, ε'', parts:

$$\varepsilon' = \varepsilon_\infty + \frac{(\varepsilon_s - \varepsilon_\infty)[1 + (\omega\tau_0)^{1-\alpha}\sin(\alpha\pi/2)]}{1 + 2(\omega\tau_0)^{1-\alpha}\sin(\alpha\pi/2) + (\omega\tau_0)^{2(1-\alpha)}} \quad (2)$$

$$\varepsilon'' = \frac{(\varepsilon_s - \varepsilon_\infty)(\omega\tau_0)^{1-\alpha}\cos(\alpha\pi/2)}{1 + 2(\omega\tau_0)^{1-\alpha}\sin(\alpha\pi/2) + (\omega\tau_0)^{2(1-\alpha)}} + \frac{\sigma}{\omega\varepsilon_0} \quad (3)$$
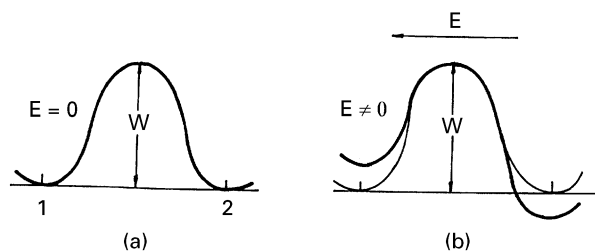
Figure 1 Potential barriers when (a) a dc voltage equal to zero is applied to the sample and (b) a dc voltage different from zero is applied to the sample.

Using Equations 2 and 3, the tangent angle of the dielectric losses, tan δ, may be expressed as follows:

$$\tan \delta = \varepsilon''/\varepsilon' \tag{4}$$

If the dc conductivity is neglected, the maxima in $\varepsilon''(\omega)$ and $\tan \delta(\omega)$ are determined, respectively, by the frequencies:

$$\omega_{\varepsilon''_{max}} = 1/\tau_0 \tag{5}$$

and

$$\omega_{\tan \delta_{max}} = \frac{1}{\tau_0}\left(\frac{\varepsilon_s}{\varepsilon_\infty}\right)^{1/2(1-\alpha)} \tag{6}$$

If however the dc conductivity is significant then a maximum cannot be observed.

3. Experimental procedure
3.1. Preparation of the specimens
The vanadium phosphate glass specimens for the measurements were produced at the Institute of Physics, the Slovak Academy of Sciences, Bratislava. The basic glass composition consisted of 70 mol % V_2O_5 and 30 mol % P_2O_5. To this composition, 1 wt % of CuO was added. The mixture was thoroughly mixed and then melted in a revolving furnace at 900 °C for 3 h. The measurement specimens were made by following the pouring technique described by Miklos [10]. In order to avoid stresses within the material, specimens in the form of pills were annealed in the air at 300 °C for 1 h. After the annealing, the specimens were ground using a fine paste and finally cleaned and polished, so that their final thickness was about 0.7 mm. After this treatment, NiCr alloy electrodes were deposited using chemical vapour deposition technology.

3.2. Measurements
The capacitance C and ac conductance G of the specimens were measured using a General Radio 1621 transformer bridge. The transformer bridge enabled the measurement of these quantities whilst using combined voltages. The measured quantities enabled the calculation of the relative permittivity, $\varepsilon' = C/C_0$ (C_0 is the geometric capacitance of the electrode system), tan δ (equal to $G/\omega C$) and the loss permittivity $\varepsilon'' = \varepsilon' \tan \delta$. The values for the dc voltages were

chosen within a range of 0–65 V, while the ac voltage was held constant at a value of 0.5 V. In order to avoid inaccuracies caused by the time dependence of the capacitance and ac conductance, the dielectric quantities were recorded one minute after the dc voltage was applied to the specimens.

Measurements at different temperatures were made in a thermostat with double thermal insulation and with inner air circulation. Using this arrangement, air temperature fluctuations in the thermostat were held to within ± 0.1 K.

4. Results
The frequency dependency of ε' at 22 °C is shown in Fig. 2. The dc voltages of 0, 30, 45 and 65 V that contributed to the combined voltage affect the observed dependency. This figure shows that ε' decreases with increasing the frequency of the ac voltage and also with increasing dc voltage. The decrease is remarkable especially at low frequencies, i.e., in the range from 10–100 Hz. At frequencies greater than 400 Hz, ε' only weakly depends on the frequency and no dependence on the dc voltage is observed.

Fig. 3 shows the dependence of ε' as a function of frequency for three different temperatures of 22, 65 and 110 °C and for two dc voltages, 0 and 65 V. According to this figure ε' increases with increasing temperature, particularly at low frequencies.

The dependence of tan δ on frequency for dc voltages of 0 and 65 V and temperatures of 22, 65, and 110 °C is illustrated in Fig. 4. From these dependences it is evident that the investigated structure NiCr/V_2O_5–P_2O_5/NiCr exhibits dielectric losses mainly at low frequencies and at high dc voltages. The influence of the dc voltage on tan δ becomes more apparent with decreasing the frequency. The polarization maximum of tan δ is nearly independent of the dc voltage, whilst a rise in the temperature causes a shift of the maximum in tan δ to higher frequencies.

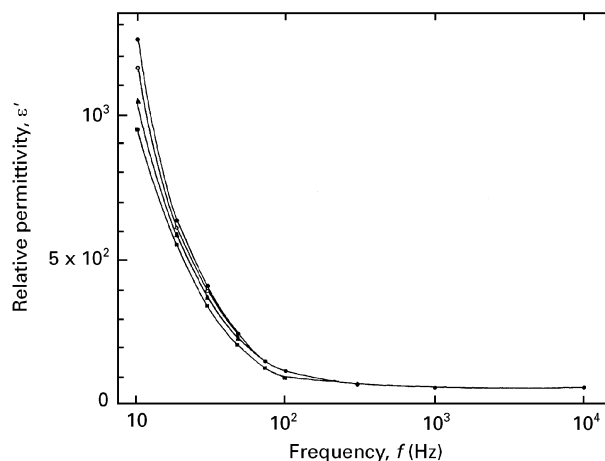*Figure 2* Variation of ε' as a function of frequency measured for combined voltages of an ac voltage of 0.5 V combined with dc voltages of; (●) 0 V, (○) 30 V, (▲) 45 V (■) 65 V. The measurement temperature is 22 °C.
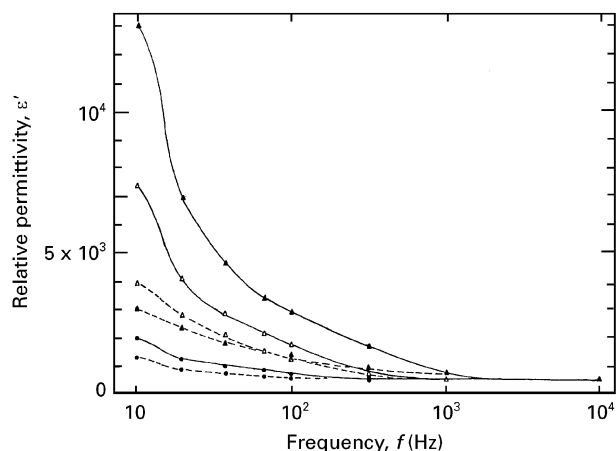
Figure 3 Variation of ε' as a function of frequency for combined voltages of an ac voltage of 0.5 V combined with a dc voltage of (———) 0 V and (-----) 65 V at temperatures of (●) 22 °C (△) 65 °C and (▲) 110 °C.
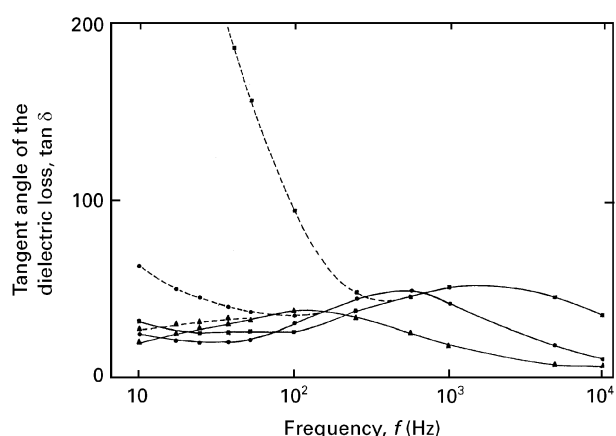

Figure 4 Variation of tan δ as a function of frequency for combined voltages of an ac voltage of 0.5 V and dc voltages of (———) 0 V and (-----) 65 V at temperatures of (▲) 22 °C (●) 65 °C and (■) 110 °C.

5. Discussion

A structural analysis of vanadium phosphate glasses with various compositions suggests that the transition metal, vanadium, participates in the generation of the glass lattice, first of all in the form of the glass-generating oxide V_2O_5. In the glass lattice, the vanadium occurs predominantly in the form of the cation V^{5+}. Due to the loss of oxygen in the melting process, the vanadium in the glass may also occur in the lower oxidation state of V^{4+}. The presence of ions with different valencies can generate electron conductivity by a hopping process which in turn leads to electron relaxation polarization.

The hopping mechanism for the transport of electric charges can be modelled in terms of a potential barrier for electron movements. The electron hops between two sites are activated by a sufficiently high thermal energy to overcome the potential barrier, however in some cases tunneling through the barrier is possible.

The charge transport indicates that in vanadium phosphate glasses only elastic and relaxation polariza-

tions and also dc conductivity take place. Due to the presence of the relaxation polarization, the permittivity of the glass decreases with an increase of the frequency (Figs 2 and 3), and the presence of a maximum in tan δ is not clearly evident.

The increase of ε' with increasing temperature (Fig. 3) can be explained by a rise in the electron concentration and due to this an enhancement of the electron relaxation polarization. The decrease of relaxation times in the corresponding relaxation processes can only occur in the case where the maximum in the tan δ versus frequency plots occur at high temperatures (if we assume, in addition, that the quantity α of the power function is effectively constant with temperature).

The simultaneous decrease of permittivity and increase of tan δ with the rise of dc voltage (Figs 2–4) can be explained by a deformation of the potential barrier by the dc voltage (Fig. 1b) which lowers the effective height of the barrier and, hence increases the transition probability of the charge carriers through the barrier.

The values of ε' measured in our structure $NiCr/V_2O_5–P_2O_5/NiCr$ (Figs 2 and 3) are considerably larger than those measured in the same material by other authors [1, 2]. This leads us to conclude that a barrier layer is created at the surface of the electrodes. This barrier prevents the transfer of electrons to the surface of the electrodes. The polarization corresponding to this phenomenon is known as pre-electrode, interlayer, migration or as the Maxwell–Wagner polarization. This polarization is a relaxation polarization, and because of its behaviour in electric fields, it is not distinguishable from other relaxation polarizations.

6. Conclusion

The values of the dielectric properties that we have measured show that certain vanadium phosphate glasses exhibit dielectric relaxations that to a first approximation may be described by modified Debye equations. Since the dependence of ε'' on frequency did not have a maximum in the interval in which we have made measurements, it proved impossible to evaluate the most probable relaxation time τ_0 for the polarization process in these materials. Therefore, in this paper we have only discussed a qualitative physical interpretation of our results which, however, points to a significant influence for the NiCr electrodes on the dielectric relaxation processes.

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