Reversible and irreversible electrical switching in $\text{TeO}_2\text{-V}_2\text{O}_5$ based glasses

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ABSTRACT

The switching phenomenon observed in electronically conductive glasses corresponds to a sudden decrease in electrical resistance of the sample when a large electric field is applied. A simple electrothermal model is developed which takes into account only a Joule effect overheating of the material. In a temperature range below the glass transition temperature, T_g , the switching is reversible. On the other hand, in a temperature range above T_g , a conductive crystalline phase is irreversibly formed leading to a permanent high conductivity state.

INTRODUCTION

In some electronically semi conductive glasses, an anomalous electrical behavior can exist, leading to voltage variations as a function of current, presenting a maximum voltage, the threshold voltage, followed by a negative differential resistance zone. This phenomenon has been described in the literature as the so-called "switching effect". It can be totally reversible or not. Such behavior has been encountered in chalcogenide (1) and oxide glasses (2).

Our study reports results obtained on $\text{TeO}_2\text{-V}_2\text{O}_5$ glasses, which has already been studied by Mansingh (3).

GLASS SYNTHESIS AND CHARACTERIZATION

The appropriate quantities of reagent grade V_2O_5 and TeO_2 are mixed in order to obtain a 0.4 TeO_2 - 0.6 V_2O_5 glass composition. This mixture is melted at 940°C . It is then poured into a preheated aluminum cylindrical mold and annealed at $180\text{-}190^\circ\text{C}$ for 48 hours.

X-ray diffraction analysis of the samples shows no evidence of crystalline phases and the differential thermal analysis diagram indicates that the glass transition occurs around 240°C , followed by two exothermic peaks at 280°C and 310°C corresponding to two successive reactions of glass crystallization.

The annealed glass cylinder is sliced into plates of thickness between 0.3-0.6 mm and sealed with platinum paste on glass slide. Platinum paste or sputtered gold is used alternatively to form the electrodes. A thermocouple is carefully maintained at the slide surface in order to measure the temperature variations of the whole set-up. This set-up is placed in a temperature controlled cell for measurements between 213 K to 473 K.

Electrical low field impedance measurements lead to an exponential dependence of the conductivity with the reciprocal temperature in the range 213 K to 473 K:

$$\sigma = \sigma_{\infty} \exp\left(\frac{-E_a}{kT}\right) \quad (1)$$

RESULTS AND DISCUSSION

Fig. 1 - Experimental and calculated nonisothermal current-voltage characteristic curve. The overheating measured at 0.03 A is more than 30 K.

Fig. 1 shows a typical current-voltage characteristic curve obtained by use of a galvanostatic current set-up on our vitreous samples. This plot shows reversible electrical behavior presenting a maximum voltage in the studied intensity domain and is quite similar to the experimental results presented by Mansingh. Such behavior may be justified by a regular decrease of the sample's electrical resistance. This lowering is attributed to the rise in heat caused by the Joule effect. This point has been confirmed by simultaneous measurements of the set-up temperature suggesting increases which can reach about thirty degrees at high current density when the equilibrium thermal conditions are attained. This takes about 1 to 10 minutes depending on the applied intensity. A simple model is now developed as-

suming that:

(i) the temperature increase is proportional to the injected electrical power:

$$\Delta T = \alpha V I \quad (2)$$

(ii) the stationary resulting voltage is proportional to the applied current:

$$V = R(T) I \quad (3)$$

In this last expression, $R(T)$ represents electrical resistance at $T = T_0 + \Delta T$, where T_0 is the initial temperature ($I = 0$ and $V = 0$). Replacing the resistance by its temperature dependent expression (transforming Eq. 1), Eq. 3 becomes:

$$V = R_\infty I \exp \left(\frac{E_a}{k(T_0 + \alpha V I)} \right) \quad (4)$$

which gives an implicit relation between V and I . Computer least squares analysis is used to calculate the values of the independent parameters, α , R_∞ and E_a . The determined value of the dc conductivity activation energy is approximately 0.37 eV which is very close to the value measured by impedance spectroscopy (Fig. 3). The numerical curve is drawn in solid lines in Fig. 1.

Fig. 2 - Irreversible current-voltage curve.

drop observed in B-C-D corresponds to a sudden decrease of the resistance resulting from local significant overheating leading to the formation of hot channels inside which the temperature could overpass T_g . The temperature measurements monitored during these steps show a drop corresponding to a large decrease in the electrical dissipated electrical power. The E-D-A return, actually describing a new characteristic current-voltage curve, suggests that the material has been affected by an irreversible transformation associated with a conductivity increase.

The reversibility of this electrical behavior is observed as long as the characteristic parameters, α , R_∞ and E_a , remain constant, which is the case if the physical properties of the material change in a reversible manner. If at high current intensity, the rise in temperature provokes an irreversible structural modification which lead to different electrical characteristic properties, the experimental decreasing current data points will result in a different I-V curve defined by another set of parameters.

Such behavior is illustrated in Fig. 2. The experimental curve is broken up into several parts. The A-B part corresponds to a moderate homogeneous heating of the sample below its glass transition temperature, T_g and the experimental data are distributed according to Eq. 4. The voltage

Fig. 3. - Conductivity variations as a function of temperature for a glass sample heated over its glass transition temperature.

phased structure which could be the mixture of different crystalline phases (V_2O_5 and $2TeO_2-V_2O_5$ as predicted by the phase diagram) and a residual vitreous phase.

CONCLUSION

This study shows that the switching observed in $TeO_2-V_2O_5$ glasses results only from electrothermal effects for the so-called reversible mechanism and for the non-reversible one. The transition between these two different domains of behavior is caused by a partial recrystallization of the glass when the Joule overheating becomes too significant.

REFERENCES

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In order to check this assumption, we have measured by impedance spectroscopy the conductivity variations as a function of the temperature of vitreous samples heated at temperatures higher than their glass transition temperature. The main results are plotted in Fig. 3. They show a conductivity increase of around two orders of magnitude when the temperature reach the overcooled liquid domain. This increase is irreversible and the measurements carried out during a cooling stage show that the conductivity-temperature relationship is still the same as in Eq. 1, but with a smaller activation energy. The value of the activation energy is very close to the values given in the literature for crystalline V_2O_5 . These results indicate that a partial recrystallization of the material should occur. This point is confirmed by SEM analysis showing a multi-