

**SWITCHING PROPERTIES AND CRYSTALLIZATION OF  
TE<sub>50</sub> AS<sub>34</sub> S<sub>16</sub> CHALCOGENIDE GLASS**

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**ABSTRACT:**

*The Te<sub>50</sub> As<sub>34</sub> S<sub>16</sub> chalcogenide glass showed a memory behaviour. I-V results on the surface show that the activation energy for switching process is 0.648 ev. Isothermal annealing around the crystallization temperature showing that the amorphous to crystalline transformation in this glass follows a simple rate equation with energy of crystallization equal to 1.04 ev. On isochronal annealing at different heating rates, the activation energy decreases from 0.32 ev to 0.059 ev on increasing the heating rate.*

**INTRODUCTION:**

The switching process observed in amorphous semiconductors is characterized not only by the breakdown of the high resistance state of the material but very importantly by the presence of a positive feedback mechanism which provide the high conductance on-state so that the breakdown nondestructive and repetitive switching is possible. The various models proposed to explain the switching process may be categorized into homogeneous and heterogeneous models.

Many studies have been made on the switching phenomena in chalcogenide glasses and the cause of switching phenomena has been classified into those initiated thermally<sup>(1-3)</sup> and those initiated

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electronically<sup>(4-6)</sup>. Ovshinsky<sup>(7)</sup> discussed the major features of switching phenomena in  $\text{Te}_{48} \text{As}_{30} \text{Si}_{12} \text{Ge}_{10}$ . He mentioned that in the highly resistive state the switching voltage increases linearly with the thickness of the film. Mehra, et al.<sup>(18)</sup> reported the thermally initiated switching characteristic in bulk Se-Te-Ge system by measuring the I-V characteristics as a function of temperature. They found that  $V_{\text{th}}$ 's are very sensitive to the ambient temperature of the sample. Saji et al.<sup>(9)</sup> found that the value of  $V_{\text{th}}$  decreases while  $I_{\text{th}}$  increases with increasing temperature. The reversible switching phenomenon was observed and investigated in the composition  $\text{Se}_{81} \text{Te}_{19}$  of the glassy state at room temperature up to the melting temperature<sup>(10)</sup>. The measured exponential dependence of the threshold voltage  $V_{\text{th}}$  on temperature gives cause to the conclusion that  $V_{\text{th}}$  disappears at the softening temperature.

### EXPERIMENTAL

The experimental technique regarding preparation of  $\text{Te}_{50} \text{As}_{34} \text{S}_{16}$  bulk alloy has been reported elsewhere<sup>(11)</sup>. For an immediate display of I-V characteristic, a potentiometer was connected to the power supply and driven by a step motor (U.K.-M3). A digital multimeter (ITT Metrix-model) was used for monitoring the sweeping unit output voltage. An electrometer (Keithely 610C) was used for measuring the current. To measure the voltage drop across the sample, an electrometer (Keithely 155 null detector) act as a digital to analog convertor, and recording the analog voltage using the X-Y recorder (Franel-model 3500). The temperature was recorded by the aid of temperature control unit (type Digi-Sense Model Cole- Palmer with K-type sensor).

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The electrical resistance of thin flakes samples was measured as a function of temperature with the help of a fully automatic furnace and a Keithley electrometer (type 610C). A fine wire chromel- alumel thermocouple in contact of the sample and connected to a digital thermometer (Omega 2168A) was used to monitor the sample temperature.

The differential thermal analyzer (type Shimadzu DT-30) was used for isochronal annealing of 0.1g of the samples at different heating rates (5°C/min. up to 100°C/min).

### **RESULTS AND DISCUSSION**

Switching properties on the surface for bulk  $Te_{50}As_{34}S_{16}$  were studied at room temperature (300K) as a function of electrode separation by two methods: a) The distance between the two electrodes increases as the number of runs increases as shown in Figs.1, b) The electrode separation decreases as the number of runs increases (Fig. 2). The I-V characteristics exhibit an ohmic behaviour at low voltages and the current is approximately proportional to the electrode separation [Fig.3 (a)]. At voltages below  $V_{th}$ , the I-V traces becomes non-linear and above a definite voltage ( $V_{th}$ ), the sample switched to the NRS. Above  $2I_{th}$ , the current increases so rapidly that it becomes a superlinear function of V and the sample switches to the "ON" state. Fig. 3 (b) shows the relation between  $V_{th}$  and electrode separation (d). Also  $I_{th}$  is linearly increased with the surface electrode separation [Fig.3 (b)]. Fig. 3 (c) represents the variation of the threshold resistance with the electrode separation.

The current- voltage relationships on the surface of  $Te_{50}As_{34}S_{16}$  were investigated with the ambient temperature for 0.81mm

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electrode separation (Fig.4). To calculate the activation energy at threshold,  $\ln I_{th}$ ,  $\ln V_{th}$  and  $\ln R_{th}$  were plotted versus  $1/T$  as shown in Fig. 5 (a,b and c). It is noticed that  $\ln I_{th}$ ,  $V_{th}$ , and  $\ln R_{th}$  are linearly related to  $1/T$  obeying an Arrhenius relation of the form:

$$I_{th} = I_0 \exp [-E_i/KT], \quad V_{th} = V_0 \exp [E_v/KT], \quad R_{th} = R_0 \exp [E_a/KT], \quad (1)$$

The activation energies for the threshold current and threshold voltage are 0.329 eV and 0.34 eV respectively. The activation energy necessary for switching is 0.648 eV. It is noticed that the switching activation energy for the bulk (0.55 eV)<sup>(12)</sup> is lower than that on the surface with the same contact indicating a high density of defects or impurity states in the mobility gap for the bulk samples. For the surface, this is related to the lowest bond density, there are only half the electrons needed to fill the dangling states formed at the surface. Because these states are only half occupied, the surface atoms undergoes a move into the surface. Reconstruction also eliminates carriers near the surface thus pinning the Fermi energy midgap<sup>(13)</sup>. The conduction is dominated with the excitation of carriers beyond the mobility shoulders into non localized states since 0.648 eV is nearly one-half of the mobility gap for such composition. It is noticed that by increasing the ambient temperature, the system approaches the chemically ordering state with a lower free energy. This will reduce the amount of the Joule heating required for the filament path formation, So,  $V_{th}$  and  $R_{th}$  decrease with ambient temperature while  $I_{th}$  increases<sup>(14)</sup>.

The I-V characteristics showed that the negative resistance (Fig. 1,2 and 4) may be accounted for by a simple thermistor type of which

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voltage is a single valued function of current. The abrupt instability may be understood in a thermally controlled system. It appears that the thermal runaway may produce the negative resistance region. As the current increases, the formation of filament is initiated, which is simply a preferred path for easy generation and movement of carriers between the two opposite electrode. The NRS of the samples is different for the path of increasing electrode separation from that of decreasing electrode separation. This may be explained by the fact that the temperature in the path of decreasing (d) is higher than that in the path of increasing (d) so that lower applied voltage is required to maintain the temperature in the path.

On increasing or decreasing electrode separation, the threshold voltage for a fixed configuration and geometry of electrodes depends mainly on the resistance of the sample for small electrode separation<sup>(15)</sup>. It is now thought that this negative temperature coefficient of resistance is a consequence of the rapid variation of the conductivity with fermi potential<sup>(16)</sup>. In the case of surface more energy was needed to compensate the decrease in temperature radiated to the surrounding medium but for bulk the heat loss from the bulk could be neglected.

The results show that there is a critical field ( $V_{th}$ ) below which the material remains in a low conductance state (OFF state). Above this field the Joule heating term predominates and temperature and conductivity rise rapidly is proposed therefore that thermal effects play an important part in the electrical behaviour<sup>(17)</sup>. The defects in the sample cause a change in the thermal conductivity and structure of the material. The linearity of  $I_{th}$  and  $V_{th}$  with thickness [Fig. 3 (a and b)] indicates that the current in the highly resistive state is not electrode

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limited but that the electric field is essentially uniform through the bulk of the material. From these data, two well defined regions of the OFF and NRS characteristics are presented.

To get more information about the structure an isothermal annealing process was carried out at temperatures around the crystallization temperature ( $T_c=150^\circ\text{C}$ ). Fig.6 shows a typical isothermal annealing plot and expected, the resistance drops sharply approaches a value close to the resistance of the corresponding crystalline phase ( $R_c$ ). The time  $\Delta t$  during which R approaches a constant value is found to increase on decreasing the annealing temperature.

The equation of the isothermal process is given as follows:<sup>(18)</sup>

$$\begin{aligned}\Delta t_i &= \Delta \phi_i \exp (-Q/KT_A), \\ \ln \Delta t_i &= \ln \phi_i - C'\end{aligned}\quad (2)$$

Since  $C'$  is a constant for an isothermal process, and  $\Delta t_i$  is the length of time during which the property has changed by a certain amount  $\Delta \phi_i$  and  $Q$  is the activation energy governing the process. For any given heat pulse:  $\Delta \phi_i$  is given by:

$$\begin{aligned}\Delta \phi_i &= \Delta t_i \exp (-Q/KT_i), \\ \text{or } \ln \Delta \phi_i &= \ln \Delta t_i - Q/KT_i = C'' - Q/KT_i\end{aligned}\quad (3)$$

Since  $C''$  is constant for an isocronal process.

By combining equations (2) and (3), a relation between the two experimental ways of carrying out an annealing process can be obtained.

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$$\ln \Delta t_i = C'' - Q/KT_i \quad (4)$$

Where  $C = C' + C''$

Therefore, the plot of  $\ln \Delta t_i$  versus  $1/T_i$  for different constant structures yields a straight line as shown in Fig.7, indicating that amorphous to crystalline transformation in this glass follow the simple rate equation (4) and the activation energy obtained is equal to 1.04 ev.

From the isothermal annealing, it is noticed that a sudden drop in the sample resistance value occurs at 150°C {Fig.6} which is the crystallization temperature obtained from the DTA data published before and this may be related to the formation of crystalline domains<sup>(9,19)</sup>. On further increasing of the annealing temperature, the concentration of crystalline domains increases which is supported by the fact that the resistance of such composition has been highly decreased. Therefore the transformation from the amorphous to crystalline state in the  $Te_{50} As_{34} S_{16}$  glass is a thermally activated time dependent process and hence nucleation and growth can be controlled<sup>(20)</sup>.

Fig. 8 shows the effect of heating rate on the R-T relationship using the differential thermal analyzer. It is clear that as the heating rate increases, the variation of the sample resistance with temperature becomes very small. Since the resistance of the glassy sample depends on the heat pulse (height and duration), therefore, on increasing the heating rate the duration decreases and hence the temperature increases to obtain the same effect.

On plotting  $\ln R$  vs  $1/T$  for different heating rates, the activation energy  $\Delta E$  ranges from 0.32 ev to 0.059 ev for heating rates ranging from 10°C/min to 100°C/min. This could be related to the high density

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of localized states in the gap for higher heating rates and on using slower heating rates, the material was maintained sufficiently long-time inducing phase separation due to the directional nature of the covalent bonds. A reorientation of mobile structure elements towards a more stable state took place. Hence the crystallization process is a temperature dependent process<sup>(18)</sup>. As the heating rate increases, the possibility for structural changes decreases, with no detectable variation in the resistance. Therefore, if the specimens are heated up at more higher heating rates respectively, the phenomenon is found to be completely reversible. From this studies it would appear that  $\text{Te}_{50}\text{As}_{34}\text{S}_{16}$  chalcogenide glass could be reversibly switched.

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**FIGURE CAPTIONS**

- 1- I-V characteristics of  $\text{Te}_{50} \text{As}_{34} \text{S}_{16}$  as a function of electrode separation (the distance increases).
- 2- I-V characteristics of  $\text{Te}_{50} \text{As}_{34} \text{S}_{16}$  as a function of electrode separation (the distance decreases).
- 3- The relation between the threshold parameters and electrode separations.

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- 4- I-V characteristics of  $\text{Te}_{50} \text{As}_{34} \text{S}_{16}$  at various ambient temperatures.
- 5-  $\ln I_{\text{th}}$ ,  $\ln V_{\text{th}}$ , and  $\ln R_{\text{th}}$  versus  $1/T$
- 6- Variation of the resistance with time at different constant temperatures.
- 7- The plot of  $\Delta t_i$  versus  $1/T_i$ .
- 8- Temperature dependence of the electrical resistance at different heating rates.
- 9- Plots of  $\ln R$  versus  $1/T$  at different heating rates.

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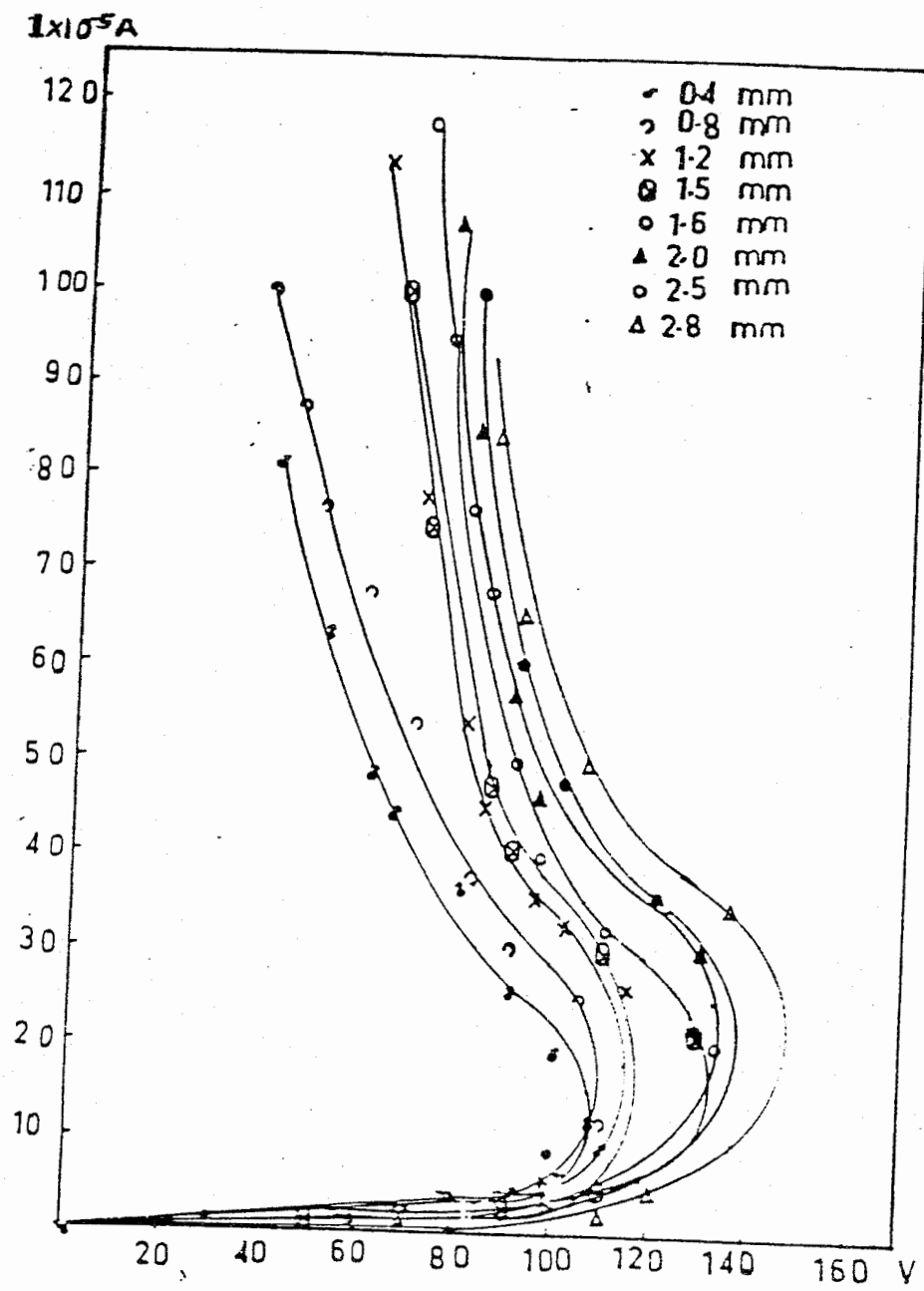


Fig. 1

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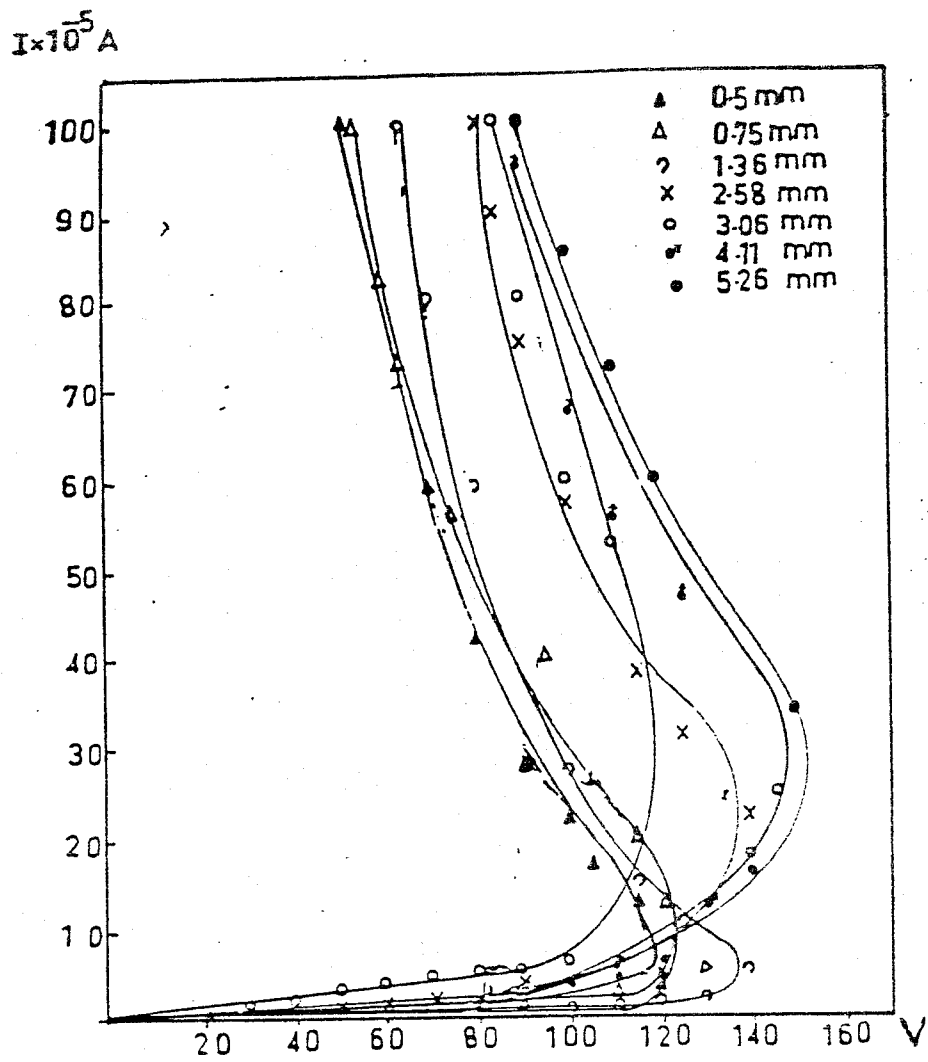


Fig. 2

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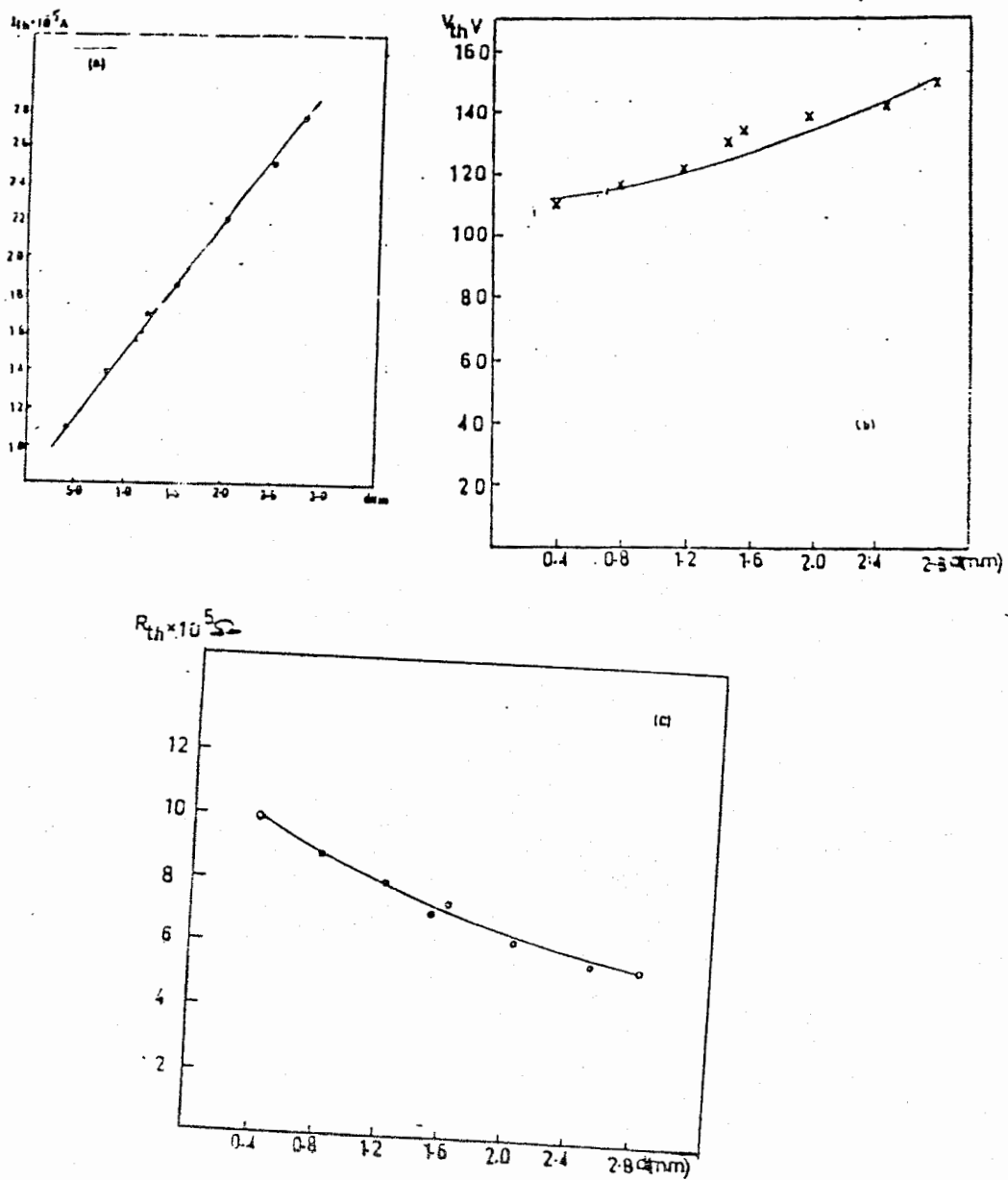


Fig. 3

A. El-Shafie

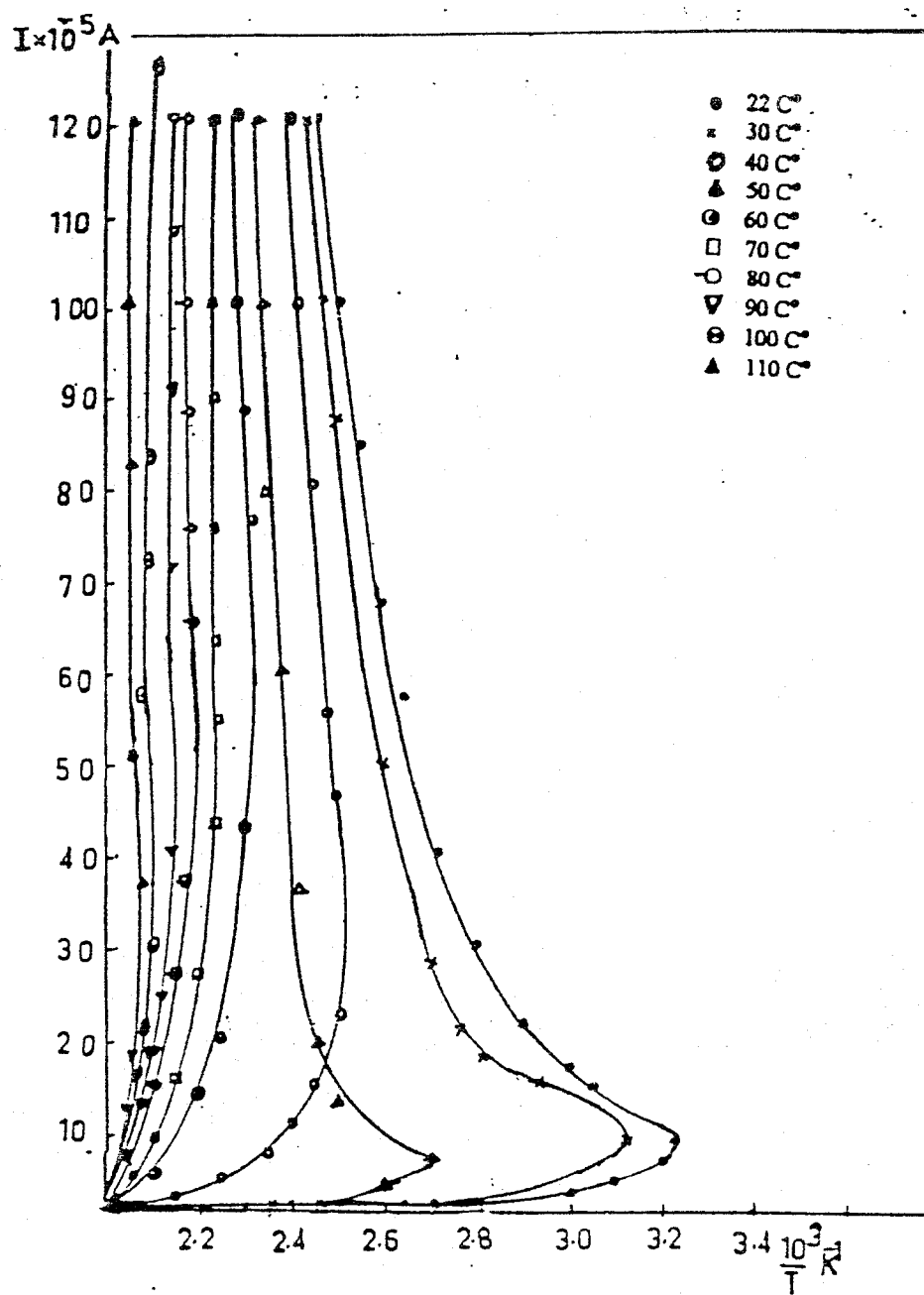


Fig. 4

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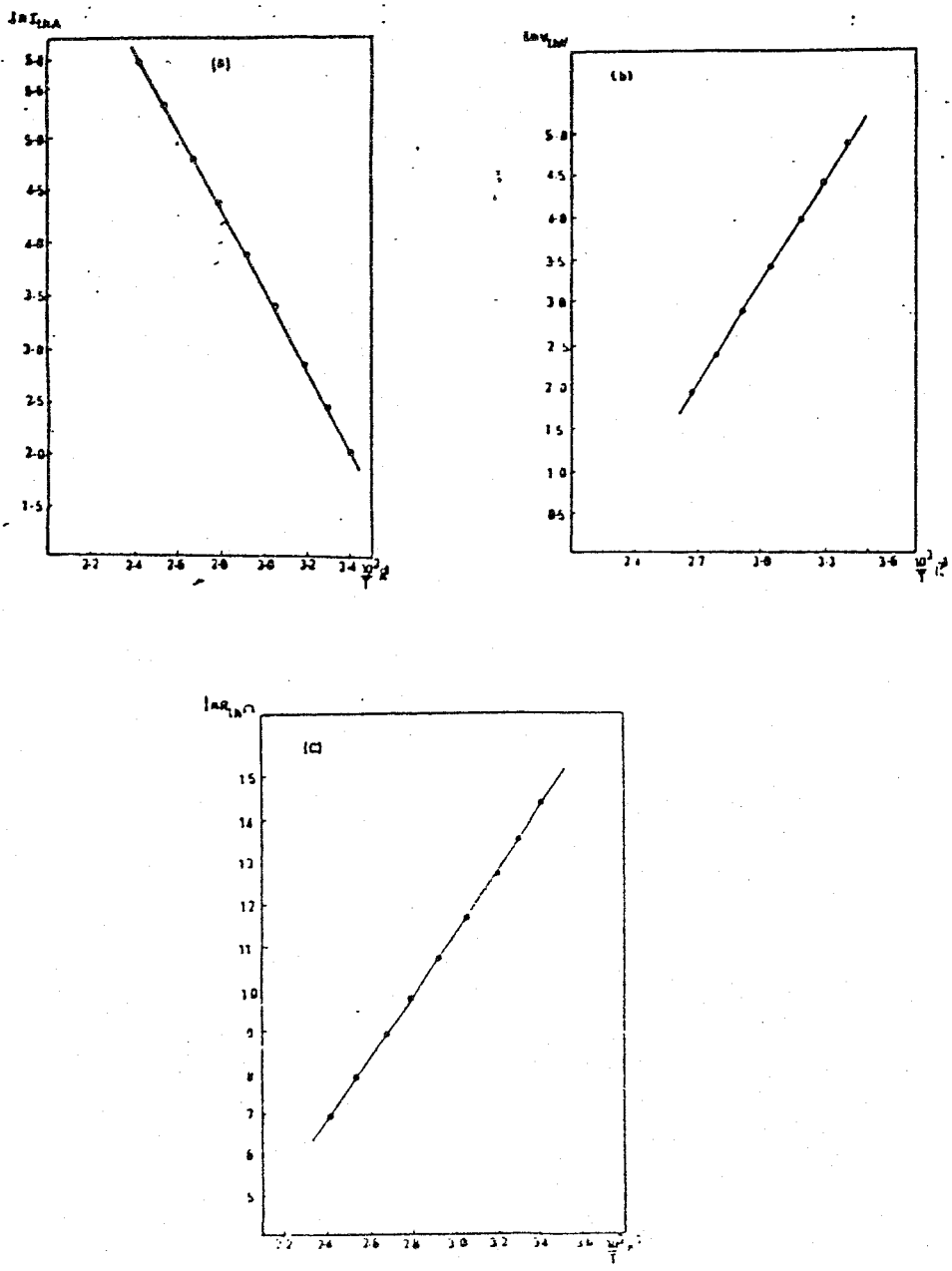


Fig. 5

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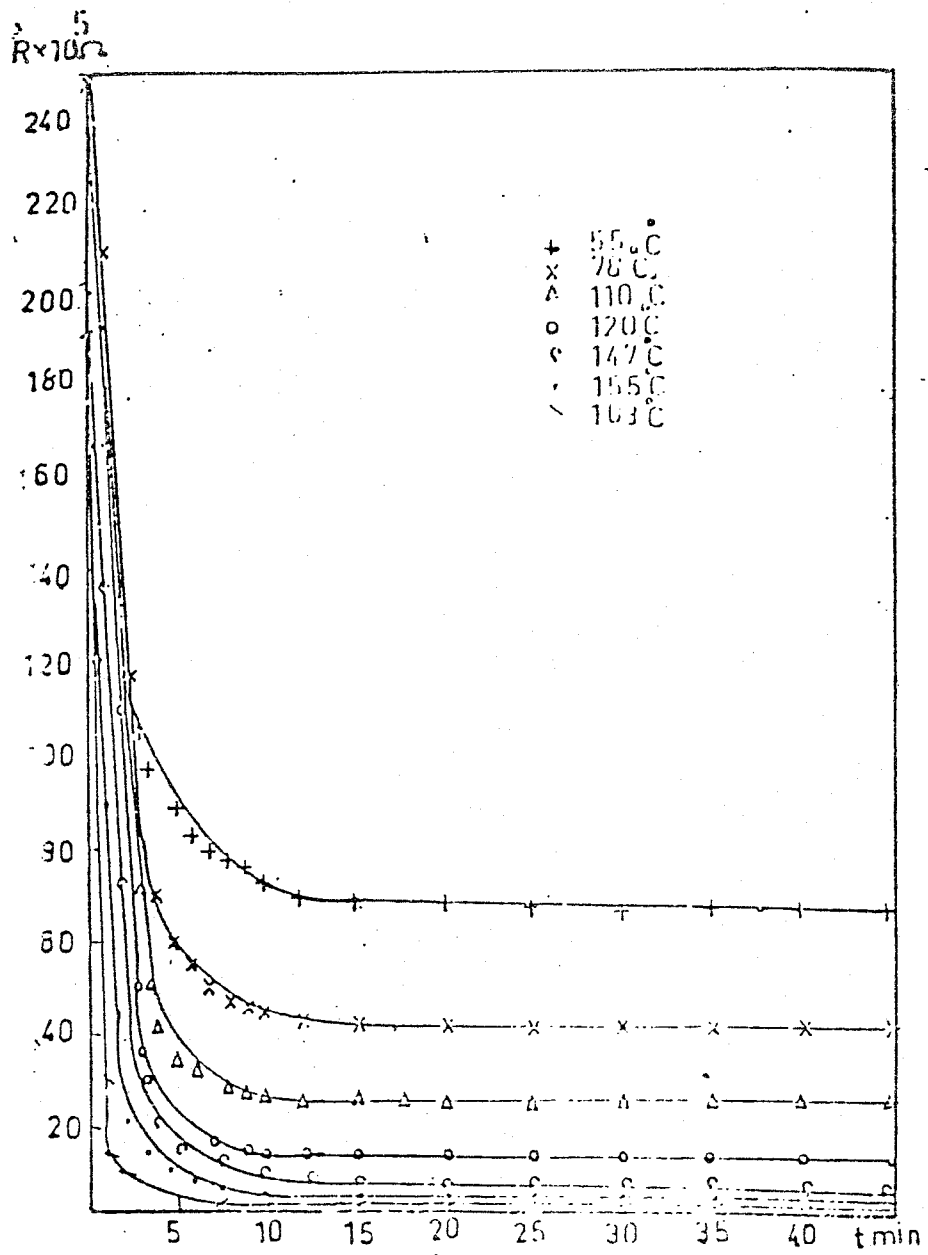


Fig. 6



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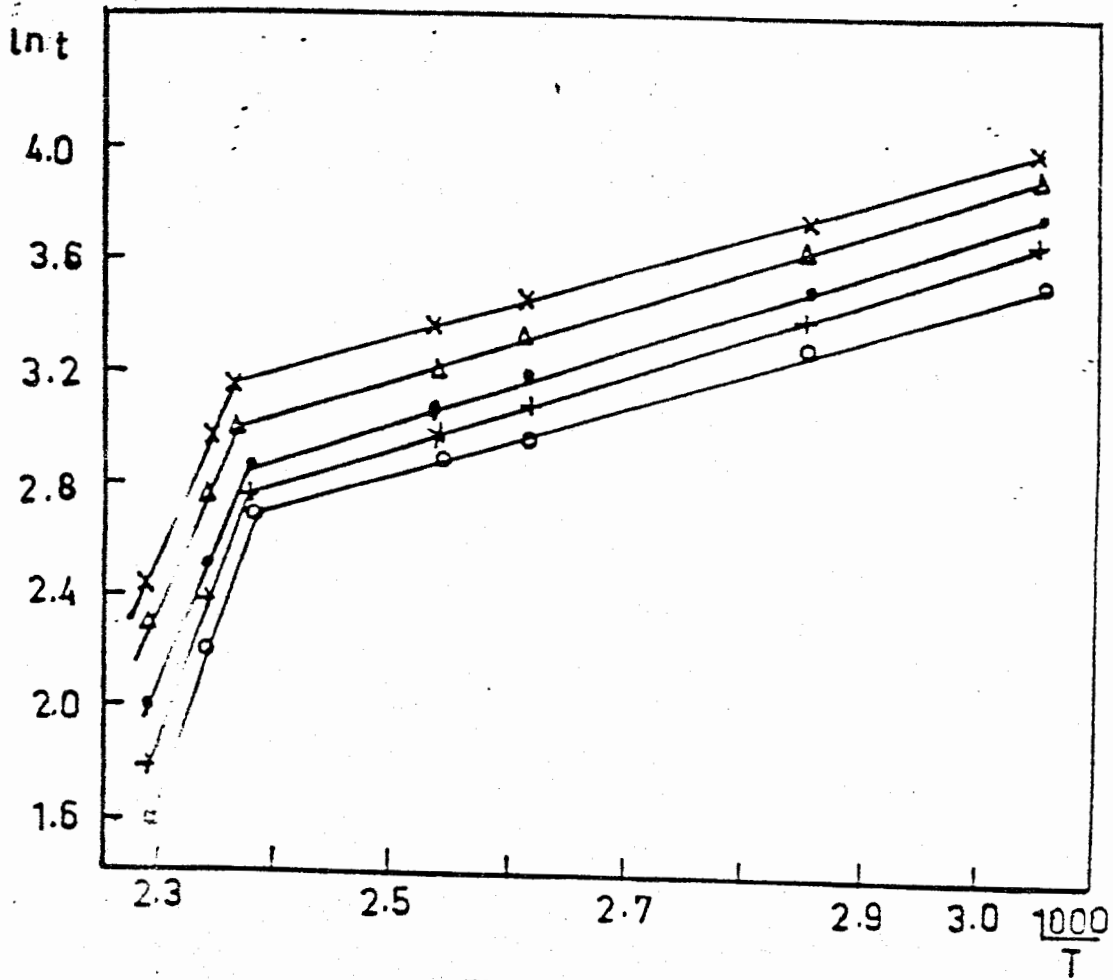


Fig. 7

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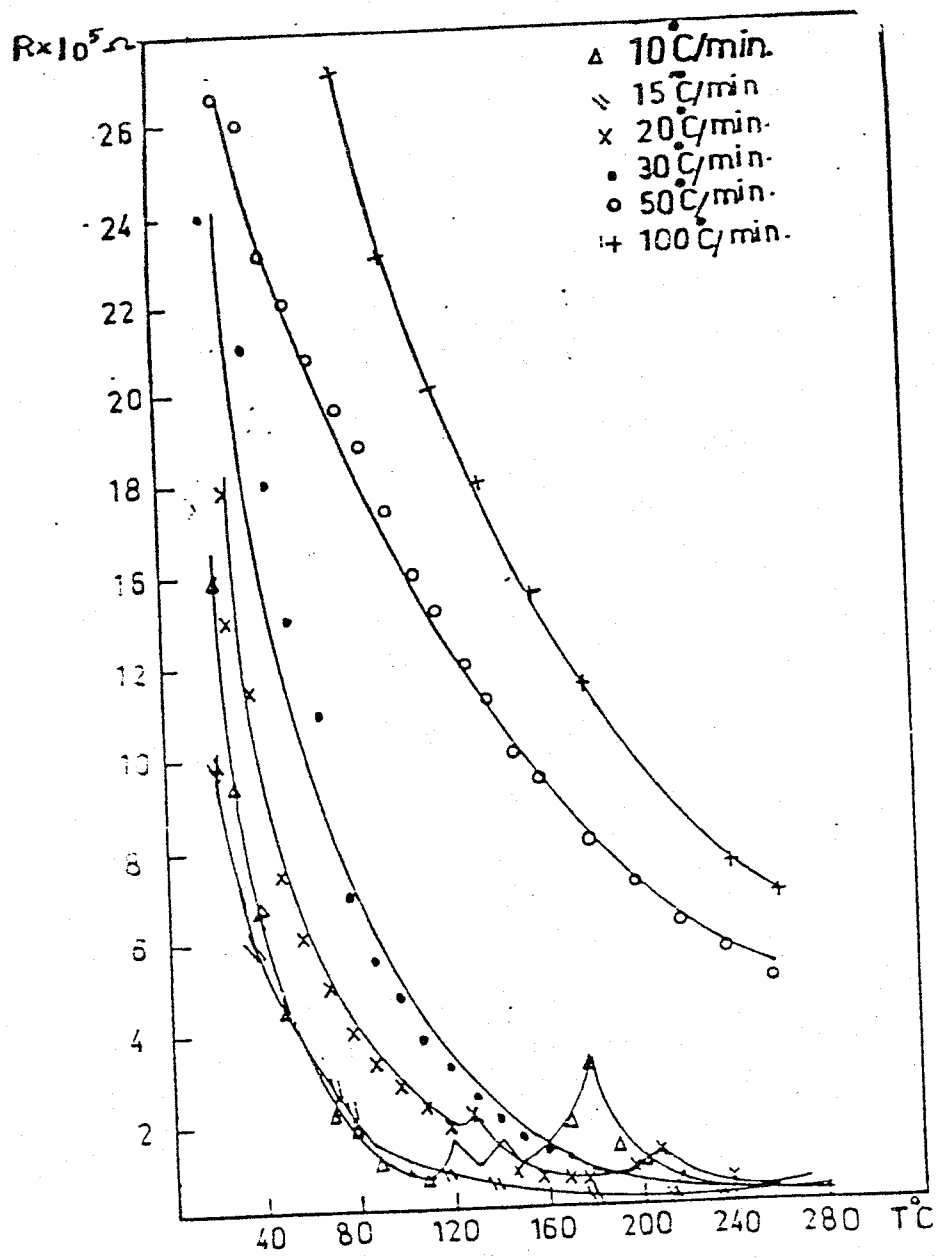


Fig.3

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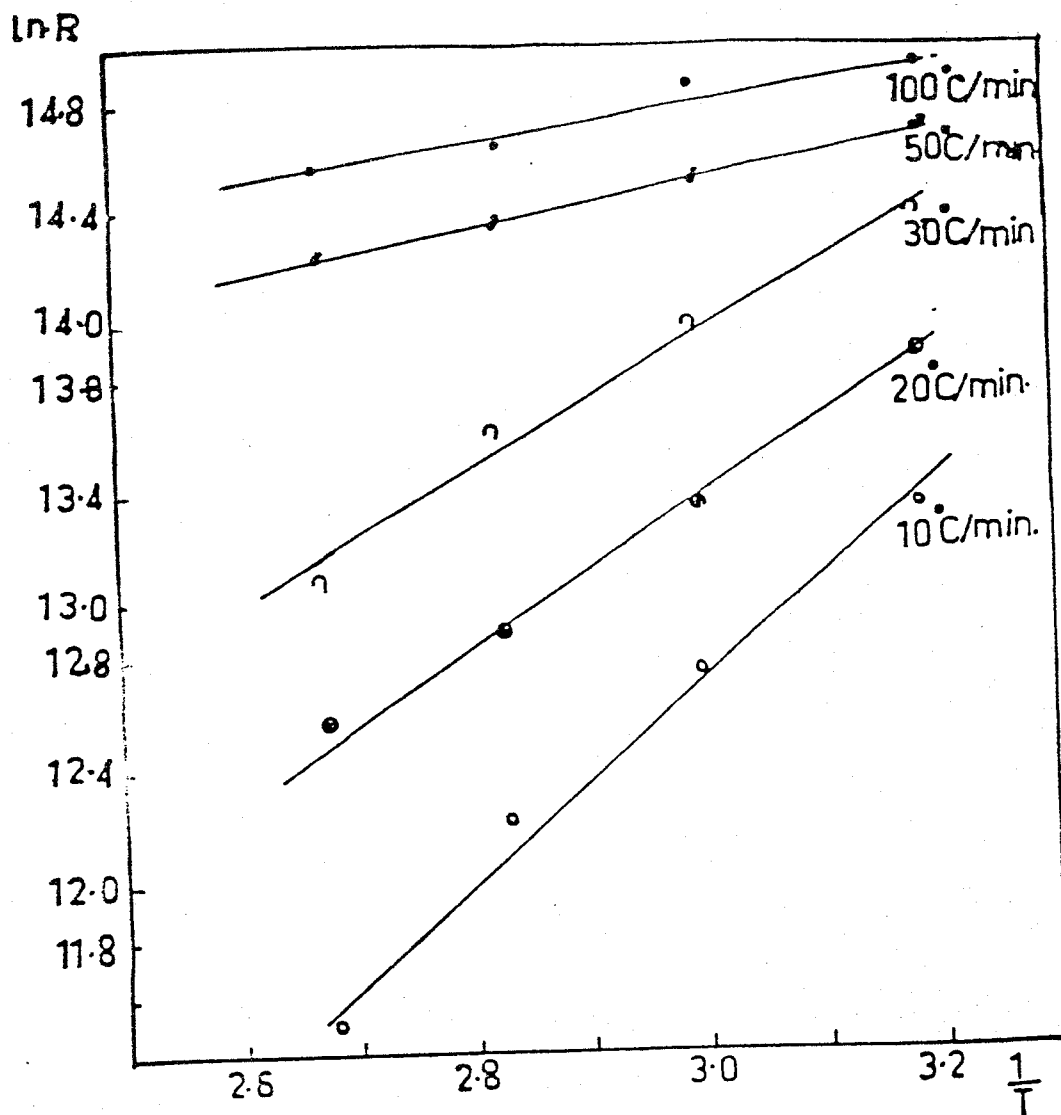


Fig. 9