

ELECTRICAL PROPERTIES OF
THICK FILMS OF A VANADIUM
PHOSPHATE GLASS



COMPUTERISED

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GENERAL INTRODUCTION

There has been an increasing interest in the study of electrical, structural and optical properties of semi-conducting glasses. These are classified into two categories: chalcogenide glasses^{1-4,31-33} and oxide glasses^{5-10,34-39}. Studies on these glasses have led to many applications in optics, electronics, etc. Particular attention is directed to their use in switching and memory devices, thermistors^{11,48,49}, etc. Vanadium glasses have found use in forming junctionless non-rectifying electronic solid switches¹², encapsulants¹³ and sealing compositions^{14,15} for semiconducting devices. Also, they are increasingly finding use as catalysts for oxidation of xylene to phthalic anhydride¹⁶, BuH, butadiene n-heptane, methyl cyclopentane, benzene and 1-butane to maleic anhydride¹⁶⁻¹⁹. Vanadium phosphate glass has been used for the synthesis of acrylic acids and esters²⁰.

In most of the publications, bulk samples in the form of pellets have been used for the study of their properties. Thick film technique, which is essentially a screen printing and firing process, has not been seriously attempted. This technique has certain advantages, particularly when glassy materials are concerned. Glass prints when fired, form good bonding with the substrate. For a glass to be a good thick film material, it should have the following properties:

- 1 : Low softening point.
- 2 : Wetting of the substrate.
- 3 : Matching coefficient of thermal expansion with that of the substrate.
- 4 : Compatibility with the electrodes.

Vanadium phosphate glass has all the above properties. The softening point is low (around 500°C); it wets alumina substrate; its thermal coefficient of expansion⁵ is of the same order as that of the 96% alumina substrates; it has been used as sealant for the electronic circuits.

In thick film technology, the films are generally 1-2 mil. thick. Vanadium phosphate glasses are highly resistive. We can use thick film method efficaciously for their study.

In the light of above observations, it was our endeavour to prepare metal-glass-metal sandwich structures by thick film method and compare the results of our study with those of bulk method.

Although Mackenzie⁸² and Higgins et al.¹⁰⁰ have used thick film method for studying switching in semi-conducting glasses, but they have not carried out other measurements like conductivity and thermo emf.

This thesis consists of the work done on the study of electrical properties of thick films of vanadium

phosphate (70 V_2O_5 - 30 P_2O_5) glass. The presentation has three parts. The first part deals with the historical survey of the subject. The second part gives the details of preparation of samples and experimental set-ups and lastly, the third part presents the results and discussion.

HISTORICAL SURVEY

Many workers (including Goryunova, Kolomiets) are of the opinion that covalent bonds are characteristic of glassy substances. On the other hand, covalent bonds are characteristics of semiconductors also. Extending these two ideas, Tarasov²¹ proposed that the glassy (vitreous) state and semiconducting properties are two aspects of the structure of a polymer whose chemical bonds are predominantly covalent.

A possible indication of a relationship between the tendency to form glasses and the semiconducting properties is the almost complete coincidence of the region where semiconductors occur in the periodic table and the region of elements which either tend to form glasses themselves or take active part in the vitrification processes. Consequently, the studies of glassy semiconductors are of special interest²². Table 1 may be referred to for comparison:

Table 1

Groups/ Periods	II	III	IV	V	VI	VII	VIII
II	Be	B	C	N	O	-	-
III		Al	Si	P	S	Cl	-
IV		Ga	Ge	As	Se	Br	-

It is now appropriate to know more about the glass and the semiconductor. In what follows, a brief description is given regarding the nature and conditions of formation of glass and characteristics of a semiconductor.

G L A S S

Glass has been variously defined²³, but most familiar one is that it is a supercooled liquid. All vitreous bodies are obtained by supercooling the melt with increasing viscosity and hardness as they cool. These properties are reversible.

Atoms in a glass are linked together by forces essentially the same as in crystals and that the atoms are oscillating about definite equilibrium positions. As in crystals, the atoms in glasses must form extended three-dimensional networks. From the X-ray diffraction patterns, it is found that this network is neither symmetric nor periodic. Yet it is not entirely random due to the fact that the inter-nuclear distances do not sink below a given minimum value.

Because of lack of periodicity, no two atoms are structurally equivalent. Isotropic nature of glass is a natural consequence of the absence of symmetry in the network. Energy required to detach will be different for each atom since they are structurally unequivalent. With increase of

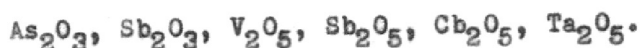
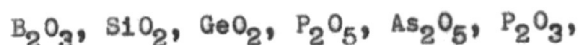
abrupt as in a crystal. Glasses possess excess of internal energy compared with crystalline substances of the same composition. From thermodynamic point of view, glass is metastable and non-equilibrium system.

Present views on the structure of glass are largely derived from the postulates of Zachariasen²⁴, later confirmed (crystallographically) by Warren and coworkers²⁷. He proposed the hypothesis of disordered network to explain the structure of silicate and borate glasses.

Zachariasen's conditions for glass formation

1. The free energy of the glassy oxide A_mO_n should not be much greater than the crystalline oxide.
2. The oxygen atom cannot be connected to more than two atoms of A.
3. The coordination number of A should be small.
4. In the network, the structural polyhedra can have common angles but not common faces/edges.

The following oxides, according to the above hypothesis, may occur in vitreous form:



where

The oxide glass of the general type must contain appreciable amounts of one or more of the following types of cations: B^{3+} , Si^{4+} , Ge^{4+} , P^{5+} , As^{5+} , Sb^{3+} , V^{5+} , Cb^{5+} , Ta^{5+} , Al^{3+} .

SEMICONDUCTOR

Semiconductors²⁵ are electronic conductors with values of electrical resistivity at room temperature generally in the range 10^{-2} to 10^9 ohm-cm. At absolute zero, pure and perfect crystals of most semiconductors would behave as insulators. The characteristic semiconducting properties (activation energy, carrier concentration, carrier mobility) are usually brought about by thermal agitation, impurities or lattice defects.

Intrinsic conduction

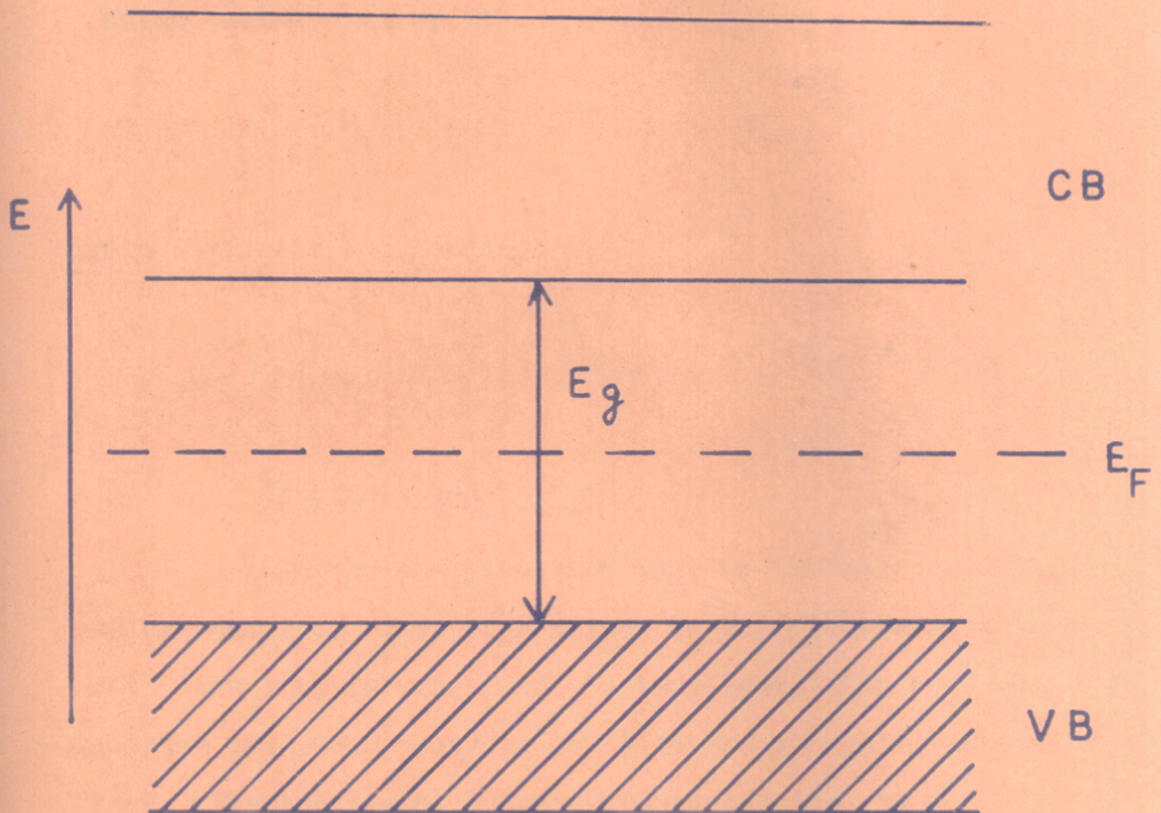
According to the band theory of solids, at absolute zero, a vacant conduction band is separated by an energy gap E_g from a filled valence band. It is shown in Fig. 1.1.

As the temperature is increased, electrons are thermally excited from the valence band to the conduction band. Both the electrons and vacant states (holes), left behind in the valence band, contribute to the electrical conductivity,

$$\sigma = |e| (n_e \mu_e + n_h \mu_h)$$

where n_e , n_h are concentrations of electrons and holes, μ_e , μ_h

FIG.1.1 BAND SCHEME FOR INTRINSIC
CONDUCTIVITY



CB—VACANT CONDUCTION BAND

VB—FILLED VALENCE BAND

E_g —ENERGY GAP

E_F —FERMI LEVEL

For an intrinsic semiconductor, $n_e = n_h$ as the thermal excitation of an electron from the valence band leaves behind a hole, then

$$(n_e)_i = (n_h)_i = 2 \left(\frac{2\pi kT}{h^2} \right)^{3/2} (m_e m_h)^{3/4} e^{-E_g/2kT}$$

then intrinsic semiconductivity

$$\sigma_i = 2|e| \left(\frac{2\pi kT}{h^2} \right)^{3/2} (m_e m_h)^{3/4} e^{-E_g/2kT} (\mu_e + \mu_h)$$

Extrinsic conduction

Silicon and germanium are the two semiconductors widely studied. They crystallize in the diamond structure with each atom forming four covalent bonds with each of its nearest neighbours corresponding to the chemical valence of four. The bonds make tetrahedral angles just as C-H bonds in CH_4 . If an atom of valence five is substituted in the lattice of silicon, one valence electron is left over after four covalent bonds are established. This extra electron can easily be excited to the conduction band. These impurity atoms which may be ionized to give up an electron are called donors and the resulting material is called n-type semiconductor.

Instead of a pentavalent atom, if a trivalent atom

the resulting material is called p-type semiconductor. On becoming ionized, the trivalent atom takes up an electron from the valence band, the hole moving to the former state of the valence electron and thus contributes in the conduction mechanism.

The above situations are shown in Fig. 1.2 and the band diagram is shown in Fig. 1.3.

Early work on the electrical properties of glasses was confined to their study as insulating materials. The resistivity range varied upto 10^{19} ohm. cm.

J. T. Littleton and G. W. Morey²⁶ have described the work done prior to 1930 in their well-known monograph on the "Electrical Properties of Glass". Later, Morey summarized this work and included the work done upto 1954. The glasses studied were insulating materials and were from the mixtures of the oxides selected from SiO_2 , B_2O_3 , MgO , PbO , ZnO , Na_2O , K_2O , CaO , BaO , MnO , Al_2O_3 , Fe_2O_3 , etc. Resistivity of soda lime glass, pyrex and lead glasses has been studied as a function of T from 50°C onwards. There is a linear relationship for $\log \rho$ vs $1/T$ in these glasses. Resistivity of the samples from A. C. measurements match with those of D.C. values in the temperature 140°C - 250°C . But below 140°C , A.C. values become lower indicating an additional loss component. This effect was seen to increase with frequency remarkably between 60 to 3000 Hz . The higher the frequency, the higher the temperature at which the additional loss was noticeable.

FIG.1.2 INTRODUCTION OF HOLES OR
ELECTRONS BY AL OR P IN SILICON

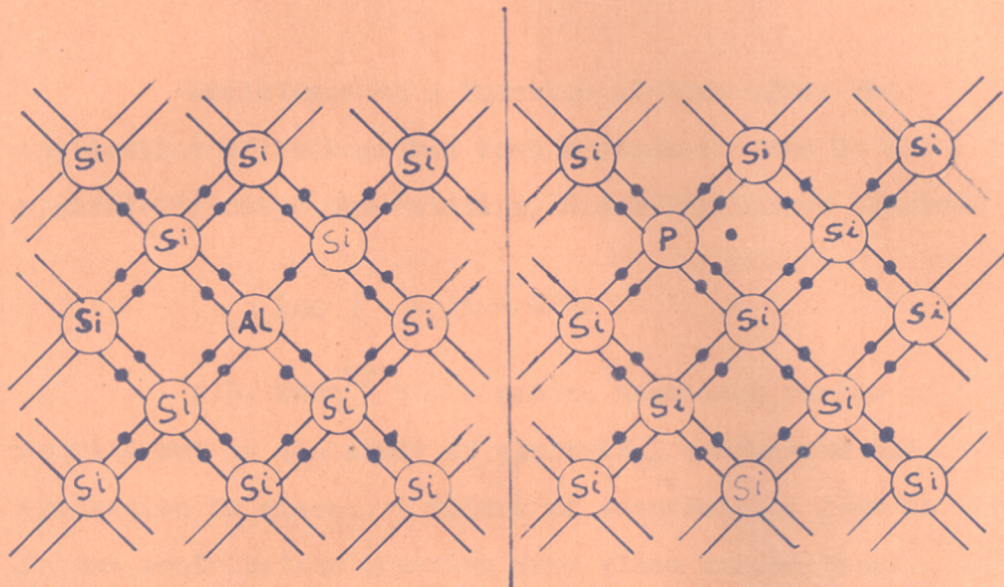
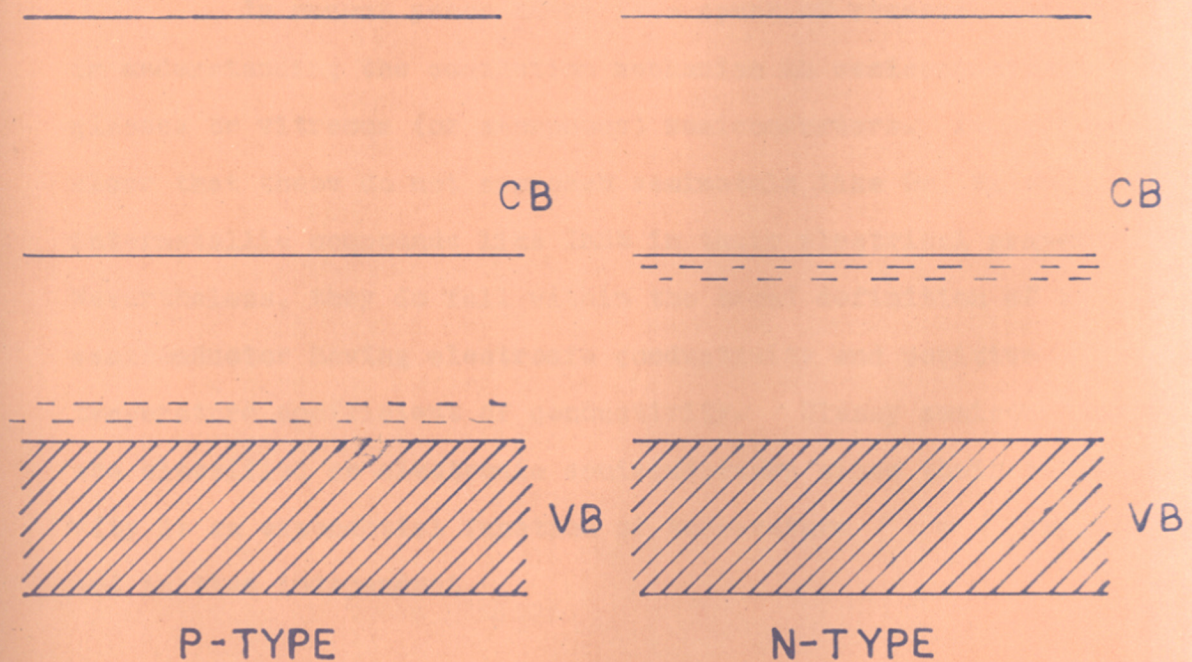


FIG.1.3 BAND DIAGRAM OF P-TYPE
AND N-TYPE SEMICONDUCTOR



Resistance as a function of time after the application of voltage has been presented. The D. C. resistivity obeys the relation, Rasch-Hinrichsen equation

$$\log \rho = A + B/T.$$

A.E. Owen²⁷ has given an excellent review of the work carried out on the study of electrical conduction and dielectric relaxation in glass. A volume of experimental data is provided in the contribution covering many glass compositions. Applications of techniques of solid state physics and chemistry, establishment of theories of relaxation phenomena and conduction mechanisms in glasses is a recent trend in research.

Semiconducting glasses

In recent years there is a spurt of research activity in understanding the conduction mechanism in semiconducting glasses or vitreous (or amorphous) semiconductors. It must be clear that these do not approach semimetals like Ge, Si or intermetallic compounds like InSb in their electrical properties. Nevertheless, they do fall within the broad definition of a semiconductor having electronic conductivity and positive temperature coefficient of conductivity. Glassy semiconductors are classified as electronic semiconductors since their resistivity is an exponential function of temperature $\rho = \rho_0 \exp.E/kT$

Semiconducting glasses can be classified into (1) chalcogenide based glasses in which one or more of the elements S, Se or Te are combined with one or more of the elements P, As, Sb, Tl or Bi. This group has been mostly studied by Russian workers¹⁻⁴.

Spear²⁸ reported electron and hole mobility measurements for both crystalline and vitreous states of selenium. He concluded that the hole mobility and corresponding activation energy were same in both the vitreous and crystalline states. Lamyon²⁹ and Hartke³⁰ studied the deeper trapping states by the techniques of space charge limited current measurements. The low field conductivity of amorphous selenium film is in the range of 10^{-4} to 10^{-16} ohm⁻¹ cm⁻¹.

Goryunova, Kolomiets³¹ and Vengel and Kolomiets² made comparative studies of the electrical properties between vitreous and crystalline states of some chalcogenide glasses. They concluded that temperature dependence of conductivity in the class of vitreous semiconductors obeys an equation of the same form as the Rasch-Hinrichsen equation. Vengel and Kolomiets² and Uphoff and Healy³² measured thermoelectric effect in vitreous compositions (As:Se:Te and As:S:Tl) and they found the chalcogenide glasses to be p-type always, whereas, Kolomiets and Nazarova³³ reported, from Hall effect measurements, that the Hall coefficient was negative indicating n-type

(2) Oxide Semiconductors

Many transition metal oxides form glasses when melted with P_2O_5 ³⁴. If the transition metal ion is capable of existing in more than one valence (oxidation) state, as in the case of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Mo and W, then the glass is semiconducting. Conduction occurs through electron transfer from low to high valence states. Conduction process has been the subject of many investigations. Vanadium phosphate glasses are one of the most extensively studied transition metal oxide glasses³⁴⁻³⁹.

Preparation of vanadate glasses was first reported by Roscoe⁴⁰ more than 100 years ago, later by Tammam⁴¹ and Stanworth⁴². Vanadium pentoxide happens to be the only oxide in the transition metal series known to promote glass formation in large quantities without the presence of glass forming oxides⁴³.

Denton et al.⁵ first reported the measurements of electrical conductivity of several vanadate glasses. The $\log \sigma$ vs $1/T$ curve was linear for the three compositions studied:

I	90% V_2O_5	- 10% P_2O_5
II	83% V_2O_5	- 9% P_2O_5 - 8% PbO
III	83% V_2O_5	- 9% P_2O_5 - 8% BaO .

for the composition I was 0.76 eV. The effect of addition of third oxide to the vanadium phosphate glass was lowering of conductivity. Effect of PbO addition was more pronounced than that with BaO.

Baynton et al.⁷ made a more systematic study of electrical conductivity of the glasses in the systems:

A : BaO - V₂O₅ - P₂O₅ and

B : Na₂O - BaO - V₂O₅ - P₂O₅.

Ohmic contacts were established by vacuum depositing gold electrodes. I-V characteristics were linear upto 1500 V/cm. applied voltage. They have reported that heat treatment of the samples had no effect on their electrical properties. The conductivity of all their glasses lay within the limits set by the compositions of Denton et al.⁵. Conductivity increased with the increase in V₂O₅ concentration. The activation energies were in the range of 0.35 - 0.40 eV for all glasses. At any given temperature and V₂O₅ concentration, the effect of Na₂O was to increase conductivity, but not in proportion to Na₂O concentration. They suggested that Na₂O could be disturbing the V⁴⁺/V⁵⁺ ratio as the reason for this effect. They did not observe any polarization effect, showing the absence of Na⁺ transportation.

Munakata et al.⁴⁴ studied the effect of V^{4+} on σ of high vanadium phosphate glasses. The system they studied was $V_2O_5 - P_2O_5 - BaO$. The plot of specific resistance to BaO/P_2O_5 had a maximum that shifted towards higher values of BaO/P_2O_5 . V^{4+} concentration decreased with increase in BaO/P_2O_5 and the total vanadium. The electrical conductivity was attributed to valence exchange between V^{5+} and V^{4+} ions.

He later⁴⁵ investigated the effect of composition and melting conditions on the conductivity of vanadium phosphate glasses containing BaO , PbO , Tl_2O or other oxides of the group I or II. He demonstrated the existence of V^{4+} as the lower valence state of vanadium which was present upto 40% in the glasses. He also found that ρ had a minimum value when V^{4+}/V total was 0.1-0.2, irrespective of the nature of the third oxide. He correlated this minimum with the cationic field strength Ze/a^2 of the added element (Z , the charge on the cation and ' a ' the mean distance between each oxygen and cation). From thermoelectric measurements, he showed that the conduction was always n-type in the glasses.

Kitaigorodskii et al.⁴⁶ confirmed that the lower valence state of vanadium was V^{4+} only and not V^{3+} or V^{2+} . They prepared specimens by reacting 80% V_2O_5 + 20% P_2O_5 with various amounts of lamp black. They studied the electrical properties of the glasses. They also found that there was no change in

Grechanik et al.²² investigated the preparation and properties of the glasses in the system $V_2O_5 - P_2O_5 - RO_x$ where RO_x represents 35 oxides of the groups I-VI. Glass forming regions were determined for 30 compositions. They measured the usual properties of semiconductors. Although they studied the properties of a large number of compositions, nothing new was found.

When $VO_{2.5}$ was replaced by Group II oxides (CaO , BaO , SrO), greatest reduction in σ occurred, whereas smallest reduction occurred when Group I oxides were used. Introduction of oxides of the elements of sub-groups 'A' lowered σ more strongly than the oxides of the corresponding elements of sub-groups 'B'.

It is interesting to note the effect of the composition on the thermoelectric power of the samples. It was found to be practically independent of temperature between $20^\circ - 200^\circ C$. In glasses containing $> 50\%$ V_2O_5 , thermoelectric power ranged from $+400$ to $-160 \mu V/degree$. When $VO_{2.5}$ was substituted by Sb_2O_3 , keeping P_2O_5 constant, the thermoelectric value decreased and eventually became negative. Grechanik et al. considered that this indicated the presence of both electrons and holes with the ratio of their mobilities being affected by the glass compositions.

Taffe et al.⁴⁷ studied the systems $V_2O_5 - P_2O_5$,

deposited silver electrodes for contacts. Relation of conductivity-temperature and of conductivity- V_2O_5 concentrations were observed to be on the same lines as before. BaO was considered to be a filler altering the V to P ratio. $\log \sigma$ and activation energy were found to depend on V_2O_5/P_2O_5 ratio.

When $V_2O_5/P_2O_5 \leq 2$, the activation energy fell rapidly and σ increased with the increase of this ratio.

When $V_2O_5/P_2O_5 \geq 2$, activation energy was practically constant and the σ increased at a slower rate with the increase of this ratio. The samples were n-type semiconductors. Conduction mechanism also was reported to be same as described by earlier workers⁷.

Munakata⁴⁸ patented the use of V_2O_5 - P_2O_5 as thermistor composition. The specific resistance varied from 10^3 to 10^4 ohm-cm depending on the composition. The system he studied was $60 V_2O_5 : XRO : (40-X) P_2O_5$ where $X < 25$ mole % alkaline earth oxide. The temperature coefficient of conductance was 2-6% per degree.

Toa Denpa Kogyo⁴⁹ studied the system $75 V_2O_5 - 5 Cs_2O - 20 P_2O_5$ for thermistor application.

Azarov and Baladina⁵⁰ studied mobility of V in the glasses of the system $Na_2O - P_2O_5 - V_2O_5$.

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Roeder and Friedberg⁵¹ made a comparative study of the σ of the two systems $V_2O_3 - P_2O_5$ and $V_2O_5 - P_2O_5$. The V_2O_5 content in both the systems ranged from 60-90 mole %. Resistivity of V_2O_3 glasses was significantly lower for higher vanadia content and V_2O_5 glasses exhibited lower resistivity for low vanadia content.

Grishina et al.⁵² measured the specific resistance and activation energy of the glasses of the two systems:

A : $V_2O_5 - BaO - PbO$

B : $WO_3 - MoO_3 - V_2O_5$.

Melnik⁵³ studied the water stability and σ of $P_2O_5 - V_2O_5 - ZnO$ system of glasses. These properties increased with increase in V_2O_5 content of the semiconductor glasses.

Matreev⁵⁴ et al. carried out similar studies as Ioffe⁴⁷ of the properties in relation to V_2O_5 / P_2O_5 ratio for the system $V_2O_5 - CdO - P_2O_5$. The coefficient of thermal emf was 100-350 $\mu V/degree$. σ increased with V_2O_5 content, also at constant V_2O_5 concentration, σ increased with increase in CdO. Log σ was found to have exponential dependence on temperature.

When $V_2O_5 / P_2O_5 < 2.5$, log σ sharply decreased and activation energy increased.

B. V. J. Rao⁵⁵ studied the system $\text{GeO}_2\text{-P}_2\text{O}_5\text{-V}_2\text{O}_5$ in depth. He reported that different atmospheres during melting had differently affected the properties. He established the glassy nature of the compositions by X-ray. The $\log \rho$ vs $1/T$ was linear upto 100°C . He observed that the slope of the curve decreased with increase in V_2O_5 content. Activation energy for 70:30 ($\text{V}_2\text{O}_5 : \text{P}_2\text{O}_5$) glass was 0.38 eV.

σ increased with the increase in V_2O_5 content. The deviation of straight line relation was significant at higher concentrations of V_2O_5 and the point of inflection of the curves occurred at 60-70% V_2O_5 . Hall mobility and Hall coefficient were calculated, $\mu = 2 \times 10^{-4} \text{ cm}^2/\text{volt sec.}$, $R = 0.2 \text{ cm}^3/\text{coulomb}$ for a composition 95% V_2O_5 , 2.5% GeO_2 , 2.5% P_2O_5 . Thermoelectric power ranged from 0-225 $\mu\text{V}/\text{degree}$.

All glasses were reported to be n-type semiconductors.

The structure of the samples in $\text{GeO}_2\text{-V}_2\text{O}_5\text{-P}_2\text{O}_5$ was reported to be unique and unusual. The opposing forces of charge densities of P^{5+} and Ge^{4+} ions on V^{5+} ion in the ternary system make the structure to undergo volume expansion upto 60-70 mole% V_2O_5 and then volume contraction takes place on further addition of V_2O_5 .

It was established from infra-red spectral evidence that VO_6 octahedron retained its identity in all the glass compositions. Resistivity data confirmed that V_2O_5 was

responsible for conductivity and not P_4O_{10}/GeO_2 . Therefore, VO_5 octahedron was considered to be the fundamental unit in the conduction mechanism. Two possible mechanisms were suggested:

- 1 : $O^{2-} \rightarrow O^- + e^-$, conduction due to electrons released by partial dissociation of oxygen ions.
- 2 : Conduction by electron exchange between different valence states of vanadium cations occupying equivalent positions in adjacent VO_6 octahedra.

The first mechanism is significant at high temperatures and the second one is important at room temperature also.

One of the conduction mechanisms suggested is as follows:

A long chain of 3-d structure of VO_6 octahedra is formed in crystalline vanadium pentoxide. In glasses, on the other hand, no such three-dimensional order exists. As V_2O_5 content decreases, this three-dimensional order is torn down from sheet structure to ribbon and finally to chain structure, depending upon the number of oxygen atoms shared by the VO_6 octahedra. These provide the paths for conduction of electrons. When VO_6 octahedra are isolated from each other, the glass becomes non-conducting. PO_4 and GeO_4 groups impair electronic conductivity in glasses.

Kent W. Hansen⁵⁶ studied the properties of iron phosphate glasses. The resistivity increased as the Fe_2O_3 was replaced by MgO . ρ passed through a minimum at a $\text{Fe}^{3+}/\text{Fe total} \sim 0.5$. Thermoelectric data showed that the samples were p-type when $\text{Fe}^{3+}/\text{Fe total} < 0.38$ and n-type at higher ratios. The results suggested that the carrier mobility was thermally activated diffusion process similar to that proposed for transition metal oxides. The conduction activation energy pertains to mobility rather than the formation of carriers. The mobilities were very low ranging from $10^{-10} - 10^{-7} \text{ cm}^2/\text{V-sec.}$ as the temperature varies from 400-600°K. The conduction was proposed to be a hopping process. Kennedy et al.⁵⁷ studied the effect of network former in semiconducting glass systems $\text{CaO-B}_2\text{O}_3 - \text{V}_2\text{O}_5$ and $\text{CaO-P}_2\text{O}_5 - \text{V}_2\text{O}_5$. They observed that thermoelectric power did not depend on the network former. Seebeck coefficient was only dependent on the carrier and site concentrations. Resistivity as a function of temperature obeyed Arrhenius equation

$$\rho = \rho_0 \exp(E/KT)$$

in the temperature range 25°-400°C. The activation energy values varied from 0.47-1.11 eV. The borate glasses had $\text{V}^{5+}/\text{V}^{4+}$ ratios higher than the phosphate glasses and therefore consequent higher resistivity values.

Bogomolova⁵⁸ carried out a combination of EPR, elec.

measurements for the samples of the systems $V_2O_5-P_2O_5-WO_3$. EPR spectra allowed the determination of W^{5+} concentration and effective mobilities of electrons in $WO_3-P_2O_5$ glasses and not V^{4+} in $V_2O_5-P_2O_5$ glasses due to their high concentration in the region for practical meaning for elec. conduction. Considerably larger mobility of basic current bearers in the value for $V_2O_5-P_2O_5$ glasses was discovered. A sharp decrease in the W^{5+} concentration was established in the case of an addition of a small amount of V_2O_5 to $WO_3-P_2O_5$ glasses.

Hench⁵⁹ studied A.C. conductivity as a function of applied frequency and temperature of the system 70 V_2O_5 : 30 P_2O_5 .

Conductivity was independent of frequency upto 5×10^4 Hz, but increased rapidly with frequency from 5×10^4 Hz to 2×10^6 Hz and was insensitive to temperature at high frequencies.

The log σ vs $1/T$ graph gave two distinct regions. At high temperature region, the slopes of A. C. conductivity vs $1/T$ are independent of frequency, comparable to that of D. C. conduction. The activation energy was 0.34 eV.

There was a marked divergence between A. C. and D.C. conduction behaviour for temperatures below 70°C.

He concluded that the mobility may, in part, be frequency sensitive. The small polaron's model concludes the existence of two additive mobility terms, μ_H (for hopping) and μ_B (for band migration).

Kolomoitsev et al.⁶⁰ observed a sharp drop in electrical conduction in the temperature region 61-71°C for the system V_2O_5 - P_2O_5 - SrO . Maximum drop occurred for the composition wherein 80 mole % V_2O_5 was present. Matreiev et al.⁶¹ studied the system V_2O_5 - Bi_2O_3 - P_2O_5 replacing ZnO by Bi_2O_3 from their earlier system⁵⁴ studied. They have not presented any extraordinary results except that the larger density values for glasses were attributed to Bi_2O_3 .

Schmid⁶² presented some new measurements and has discussed transport mechanism. He considered the small polaron as the charge carrier in vanadium phosphate glasses. A brief non-mathematical review of the theory of conduction by small polaron is presented. The polaron, he mentions, is a conceptual construct. When an electron, in its motion, occupies each site for long enough duration, the ions have time to relax into a configuration appropriate to the altered charge on the host ion. The electron and its accompanying distortion is called as polaron. If the electron overlap energy integral is large compared with polaron binding energy, it is a case of large polaron. If the linear dimensions of the polaron become

The charge transfer with exact conservation of the lattice energy is dominant in the low temperature region and charge transfer with simultaneous exchange of energy with the lattice is dominant in high temperature region. This is in agreement with Holstein's theory of polaron.

The usual theory of electronic conduction in glass is that the magnitude of conductivity depends on the ratio of bridging to non-bridging oxygen bonds in the material. This corresponds to V^{4+}/V^{5+} in the case of V-P glasses. Although the surroundings of V^{4+} and V^{5+} are different, it is assumed that the lifetime of polaron is sufficiently short that electron makes great number of transitions between possible sites in a time comparable to the relaxation time of the ligand cage.

Imanov et al.⁶³ studied the σ , thermo emf and EPR spectra of the glasses of V_2O_5 - P_2O_5 system, P_2O_5 concentration varying from 5-50 mole %. They obtained a quantitative relation between charge carrier concentration and the number of unpaired electrons. Also, the relation between the activation energy with width of EPR line was established. An electronic mechanism was found for conduction. The EPR signal increased as the P_2O_5 concentration increased.

Caley⁴³ compared the electrical conductivities of the two systems P_4O_{10} - V_2O_5 and P_4O_{10} - WO_3 glasses. The P_4O_{10} content was replaced by the oxides like SiO_2 , GeO_2 , B_2O_3 and

and TeO_2 in increasing amounts. The σ of V-P glasses was insensitive to the oxide replacement, whereas the case of tungsten phosphate glasses, σ decreased by almost 5 decades when small amount of V_2O_5 was introduced. The change was attributed to reduction of W ions.

Mathare⁶⁴ surveyed the basic properties of semiconductor glasses with respect to electronic switches and the principal differences between crystalline and glassy semiconductors. Materials discussed were: As-Te-I, Te-Ge- V_2O_5 , TeO- Al_2Te_3 -TeO, Te-Ge-Si, Te-Ge-Cs, Te-Ge-As-Ga-PbS, CaO- B_2O_3 - V_2O_5 , CaO- B_2O_3 - TiO_2 , V_2O_5 -TeO₂, As-S-Se, As-Se-Te, As-Ge-Si-Te, etc. Hench⁶⁵ studied the effect of microstructure and thermal treatment of V_2O_5 - P_2O_5 on its electrical properties. D. C. conductivity increased markedly with microstructural changes. Unusual electrical behaviour was associated with the partially crystallized glasses. In addition, A. C. absorption, elimination of high frequency conduction dispersions and inversion of frequency effects at elevated temperatures were also associated. The effect of forming variables such as quenching temperatures have been documented. A summary of the modified band theory calculations that are consistent with the above results has been presented.

Yamamoto et al.⁶⁶ reported anomalous electrical conduction in vanadate glasses. A non-linear voltage-current

response time for the negative resistance was $< 10\mu$ secs. and was faster by two orders than that calculated on the assumption of self-heating. The negative resistance became narrower as the temperature increased. Activation energy was reported to be 0.35 eV in the linear range at low voltage.

B. V. Rao⁶⁷ studied the properties of the system $B_2O_3-V_2O_5-P_2O_5$ in the vitreous and nucleated states. Some of the glass compositions displayed unusual negative temperature coefficient of resistance. I-V characteristics indicated possible thermistor applications. The infra-red spectra indicated 6-fold coordination of V_2O_5 at all concentrations.

Landsberger⁶⁸ carried out the magnetic resonance study of the $V_2O_5-P_2O_5$ glass using $51V$ NMR. Two distinctly different spectra were detected, (1) due to diamagnetic V^{5+} site, and (2) due to paramagnetic V^{4+} site. The spectral results were explained on the basis of a structural model for $V_2O_5-P_2O_5$ glass.

It was proposed that there are two units present in the glass; one is the simple VO_5 unit as in the crystalline V_2O_5 and the other has a PO_4 unit substituted for the apex oxygen of the VO_5 unit.

The $51V$ NMR spectra due to V^{4+} sites are broadened by an anisotropic hyperfine interaction. The fact that this resonance is observed suggests that the conduction electrons are localised at particular vanadium sites for a time atleast comparable to the life time of the nuclear state.

The ratio of the fractions V^{4+} and V^{5+} (n_4/n_5) present in the glass was determined from ESR intensity measurements. This decreased with the increase in V_2O_5 concentration. There is some evidence to indicate that two V^{4+} sites are formed for each PO_4 unit that is substituted for the apex oxygen of a VO_5 unit.

Davis and Mott⁶⁹ studied the conduction in non-crystalline systems. The experimental evidence concerning the density of states and the ranges of energy in which the states are localized has been reviewed. This included A.C. and D. C. conductivities, drift mobility and optical absorption. There is evidence that for some chalcogenide semiconductors, Cohen et al's model should be modified in introducing a band of localized states near the centre of the gap.

Such a band can 'pin' the Fermi level, so that the semiconductor is extrinsic rather than intrinsic. Mott made this assumption to explain the change of sign in thermopower at low temperatures in amorphous Ge. The levels being acceptors and supposed to be due to dangling bonds.

Sayer et al.³⁸ have tried to explain the influence of disorder in the glass lattice on the conduction process by taking recourse to A. C. and D. C. conductivity measurements at 77° to $420^\circ K$ and at frequencies from 100 Hz to 3.6 GHz and dielectric properties. The system they studied was

80% V_2O_5 -20% P_2O_5 . After relieving stresses in the samples by annealing at $150^\circ\text{C}/24$ hours, several metals were vacuum deposited on the glasses. Gold was found to be most satisfactory, giving ohmic contact. Al and Cr were prone to develop non-linear characteristics.

The data at low temperature was consistent with the existence of disorder energy of magnitude predicted by the equation

$$\Delta W = (e^2/4\pi\epsilon_0\epsilon' r_{maj})K$$

where, r_{maj} = average distance between transition metal ions,
 ϵ_0 = static dielectric constant,
 K = constant tabulated in Miller's paper as a function of doping concentration.

The model for A. C. conduction was similar to that of Pollack for broad band semiconductors which might be applied to polaronic materials. A. P. Martinenko et al.⁷⁰ observed short range order in adjacent ions of vanadium in the V_2O_5 - P_2O_5 -CaO system. They also confirmed the thermal nature of mechanism of switching resistance in oxide glasses containing V^{4+} ions. They have also presented EPR spectra of the glasses.

Ragen and Drake⁷¹ observed memory and switching in mixed transition metal oxide glasses. Cyclic switching of

resistance consistently within 1 ohm. The devices are capable of passing D. C. current of 1A when in ON state without either incurring physical damage or reverting to the OFF state.

Sayer et al.⁷² studied the effect of short range order on the conduction of V_2O_5 - P_2O_5 glasses. The absorption spectra showed an absorption band at 380 cm^{-1} with an intensity related to P_2O_5 and V^{4+} concentrations. EPR showed that the V^{4+} sites occur at specific structures within the glasses. A possible structure, they suggested involved a $(PO_4)^{3-}$ complex replacing a non-bonding O in the $V-O_5$ arrangement. The phonon energy corresponding to IR absorption band was 0.047 eV compared with a phonon frequency of 0.053 eV, calculated from the electrical data.

Kalygina et al.⁷³ studied the transition processes in metal-dielectric-metal structure based on the glass of the V_2O_5 - P_2O_5 system which are of interest as switches. Specimens were electrically treated to obtain the negative resistance region. The relations between the switching time from the non-conducting to the conducting state, the delay time and the restoration time for the low conductivity state, the ambient temperature and power dissipated in the specimen during current transmission were studied. The delay time changed suddenly with temperature.

They further⁷⁴ studied the I-V characteristics and attributed the change in I-V to the formation of channels,

predominantly formed by vanadium oxides whose structure was temperature dependent.

They^{75,76} probed the I-V characteristics of the systems $60 \text{ V}_2\text{O}_5 - 20 \text{ P}_2\text{O}_5 - 20 \text{ CaO}$ and $70 \text{ V}_2\text{O}_5 - 30 \text{ P}_2\text{O}_5$. Electrodes were from Ag, Al, Au, Cu, Ni or W. The electrical properties were basically same for both the systems except that the activation energy for the 3-component glass was greater than for the 2-component one.

After electroforming, the samples acquired, at room temperature, I-V characteristics with a segment of negative resistance of S-type or a symmetrical non-linear characteristic. The negative resistance as in 2-component glass was associated with the phase transitions in VO_2 grains which were formed in the channels by 1-2 orders of magnitude as the temperature was increased above 300°K . The reverse course of temperature dependence was different and was accompanied by a change in the form of I-V characteristic to symmetric non-linear.

Kuruchkin et al.⁷⁷ studied the system $70\text{V}_2\text{O}_5 - 20 \text{ P}_2\text{O}_5 - 10 \text{ CdO}$ with the DTA, EPR infra-red spectra and electrophysical properties. V^{4+}/V total increased from 0 to 0.50 as the softening temperature increased from 350° to 498°C and crystallisation temperature from $550^\circ - 640^\circ\text{C}$. The decrease in mobility of carriers was related to some strengthening of glass structure. Activation energy of

electrical conductivity was 0.25 eV at room temperature and has a tendency to decrease at low temperature.

Alexander⁷⁸ presented a paper on "Chemical Vapour Deposition of the systems $\text{CuO-P}_2\text{O}_5$, $\text{CuO-V}_2\text{O}_5\text{-P}_2\text{O}_5$ and $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$ " at an International Conference. He prepared the samples by chemical vapour deposition at $550^\circ\text{-}670^\circ\text{C}$ using CuI , PH_3 , VOCl_3 , H_2O and O_2 as the reactants. After suitable electric forming process, layers of $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$ were found to exhibit threshold switching. Glasses in the $\text{CuO-P}_2\text{O}_5$ system with Cu contacts could be switched respectively from a high to a low resistance state and back by voltage and current pulses and were electrically stable in either state.

Austin et al.⁷⁹ studied hopping conduction and optical absorption in high electrical fields in V, Fe and Mo phosphate glasses. Hopping between localised states causes a D. C. conduction of the form $\sigma = \sigma_0 [\sinh BF]/BF$ where $B = \frac{ea}{2kT}$ and a = jump distance and F = electric field. In transition metal ion phosphate glasses, excellent agreement with the above behaviour was observed except that the hopping distances were 4-7 times the lattice spacing. A model was proposed in which the effective field was enhanced at hard hops arising from the molecular structure. Optical hopping (charge transfer) under high electric fields was also examined, particularly with reference to the problem of distinguishing over-the-barrier and through-the-barrier models. New electro-absorption (EA) results are presented on charge transfer bands

in V, Fe and Mo phosphate glasses, and the EA behaviour of oxide and chalcogenide glasses near the Urbach tail is compared.

Greaves³⁶ studied the small polaron conduction in V_2O_5 - P_2O_5 glasses. Heat treatment reduced the activation energy at a given temperature which is most noticeable at low temperature. The behaviour at low temperature was described by using N. F. Mott's (1968) variable range hopping arguments and at high temperature by non-adiabatic small polaron hopping between nearest neighbours. At intermediate temperatures, a simple model was used in which excitations by optical and acoustic phonons make independent contribution to the jump frequency. The theory of N. F. Mott (1969) was extended to the polaron case for $T > 0/4$ where T is temperature and 0 , temperature characteristic of lower peak in the vibration spectrum. There was a good agreement with the experimental results. Values for the polaron radius $\sim 2.8\text{\AA}$ and the electron decay constant $\alpha = 3.5/\text{\AA}$ were consistent with the model for small polaron. The α and the d of the states at Fermi level N_{EF} were detected from the A. C. conductivity and the slope of $\ln \sigma$ vs $1/T^{1/4}$ at low temperature. Values of $N(E)$ were obtained which correlate with those obtained earlier. The disorder energy separating adjacent sites was large ~ 0.4 eV, in these materials.

Kalygina et al.⁸⁰ explained their results of switching and electrical properties of the systems containing 70 V_2O_5 -

Thermal breakdown and fusion of a narrow channel in the glass caused the formation of a polycrystalline oxide with metallic conductivity. At lower temperatures, this oxide was converted to semiconducting state to give rise to S-type negative resistance region. Reverse switching from the high conductivity to high resistance state was due to the fusion of the material in the channel and reversal to a glassy state. Depending on the electrode material, structures which can be used as switches or memory devices could be obtained.

Slack⁸¹ also observed switching in $\text{Bi}_2\text{O}_3\text{-ZnO-MnO}$ and $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$ systems. J. D. Mackenzie⁸² has made extensive review of the literature and theoretical considerations, suggested that stable threshold switches were possible. $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$ glasses were compounded in the form of an ink. Thick film technique was used to prepare the switches. A power supply system worked satisfactorily when amorphous semiconductor switches were used. Chaudhury⁸³ measured conductivity, thermoelectric power and optical absorption coefficient of $\text{V}_2\text{O}_5\text{-KPO}_3$ glasses. Electron mobility was calculated from σ and thermoelectric power data and was $2 \times 10^{-5} - 2 \times 10^{-4} \text{ cm}^2/\text{V Sec}$. The mobility activation energy was 0.372 eV. Analysis of the results led to the evidence of "pseudo gap" band model of Mott.

Mansingh et al.⁸⁴ studied the A. C. conductivity and dielectric constant at different frequencies and temperatures.

of several authors, Pollak and Gabbale⁸⁵, Pollak^{86,87}, Pike⁸⁸ have been mentioned. They concluded that annealing has no effect on conductivity, as also observed by Baynton et al.⁷. Frequency dependent A. C. conductivity of these glasses seemed to be an intrinsic property. The temperature variation of measured A. C. conductivity and the dependence of exponent ' β ' with temperature may be explained well by considering two contributions $\sigma_1(\omega)$ and $\sigma_2(\omega)$ to the measured $\sigma(\omega)$. The $\sigma_1(\omega)$ which dominates at low temperatures might be due to hopping of carriers. Second $\sigma_2(\omega)$ which dominates at higher temperatures, depending on the frequency of measurement, might be due to hopping of carriers excited to the conduction band edge (Mott and Davis⁸⁹). This was also responsible for the activated dielectric loss peaks.

L. I. Howath⁹⁰ carried out EPR investigations of V^{4+} ground state in VP glasses. Glasses based on V_2O_5 are known to have both V^{4+} and V^{5+} ions. Conductivity measurements have been quantitatively interpreted by polaron hopping. The ion core of $V^{5+}(3s^2 3p^6)$ is diamagnetic and hence cannot be detected by EPR, whereas $V^{4+}(3s^2 3p^6 3d^1)$ is paramagnetic leading to EPR absorption.

First derivative of EPR spectrum of these glasses was a singlet centered at $g = 1.960 \pm 0.001$, line width being 250 Gs. The g -factor and linewidth remained constant throughout

means that the mobile conduction electrons were localized for a time longer than the magnetic life time.

The anomalous maximum in conduction which appears with the increase in V^{4+} in the glass did not result in any change of the value of g-factor and line width. However, there was a change in hyperfine structure in glasses with a fairly low V^{4+} content in V^{5+} matrix. The nearer the V^{4+} ions were, the stronger the dipolar interaction between the V^{4+} ions. At higher V^{4+} content, the collapse of the hyperfine structure indicated that the dipolar interaction was stronger than the nuclear hyperfine structure. The temperature dependence of conduction was attributed to the changes in mobility or structural rearrangements or both.

Earlier theoretical work was carried out treating electronic conductivity, thermoelectric power etc. in liquids and amorphous solids mainly by Russian workers. Excellent review of this work may be found in Ioffe and Regel⁹¹. The general conclusion is that the spectrum of electrons in a liquid or an amorphous solid has a band structure as in a crystal and that a periodic array is not a necessary condition for the appearance of semiconducting properties. Many other authors⁹² have shown that band structure has not changed in the material in transition from a solid to liquid state. Fischer⁹³ considers that random nature of a liquid invalidates

In his review article, T. I. Barry⁹⁴ gives a clear picture of the conduction mechanism.

Although the majority of oxide glasses are ionic, rather than electronic semiconductors, electronic conduction predominates in glasses containing high concentration of transition metal ions. He mentions that the most intensively studied system is $\text{VO}_x\text{-P}_2\text{O}_5$. Here both V^{4+} and V^{5+} ions are present in the glasses, the proportion of V^{4+} declining with the increase of VO_x concentration. Reagan and Drake⁹⁵ found that the threshold voltage for transition from low to high conductivity of a partially reduced 75 V_2O_5 - 25 P_2O_5 glass was a function of temperature extrapolating to '0' at 68°C. There was also a change in expansion coefficient at this temperature which significantly is the Neel temperature of VO_2 .

Friebele et al.⁹⁶ noted that the unmixing that occurs in glasses, containing more than 65 mole % V_2O_5 was accentuated by partial reduction and suggested that the V^{4+} ions in the separated phase have local ligand's environment similar to VO_2 .

Although they may often be difficult to interpret, magnetic exchange interactions offer considerable scope for investigating the early stages of clustering in glass as exemplified by the work of Landry⁹⁷. Numerous spectroscopic techniques including X-ray, γ -ray, optical, infrared, Raman, EPR, NMR, have been used to study the valence stages, structure and molecular motion in glasses as reviewed by Wong and Angell⁹⁸.

H. Bötter and Byksin⁹⁹ have presented an excellent theoretical work on hopping conductivity in ordered and disordered solids in their review article. A large number of references have been given. They have dealt the subject which includes A. C. conductivity, hopping conductivity in strong fields, Hall mobility in the hopping region, thermoelectric power in the hopping region and also have given experimental results.

P R E P A R A T I O N
A N D
E X P E R I M E N T A L S T U D Y

PREPARATION OF VANADIUM PHOSPHATE GLASS

High purity vanadium pentoxide and phosphorus pentoxide (both Koch-Light make) were used for the preparation of the glass. Due care was taken to avoid exposure of P_2O_5 to atmospheric humidity. A capsule of P_2O_5 was opened in a dry box. Some quantity was transferred to a weighing bottle. The bottle with the contents was weighed. A small portion of P_2O_5 was transferred with a stainless steel spatula to an agate mortar. The bottle was weighed again. The difference in weight was the weight of P_2O_5 taken. V_2O_5 which was dried earlier, was taken in the ratio of 70 V_2O_5 : 30 P_2O_5 (both in mole %). Both the oxides were mixed thoroughly in distilled, dry alcohol in an agate mortar with an agate pestle in the dry box. After good mixing, the alcohol was evaporated under an infrared lamp. The dried mixture was charged into a clean vitreous silica crucible. The crucible was heated in an electric muffle furnace, whose temperature was gradually raised to $1050^{\circ}C$. It took about 4 hours to reach this temperature. The oxides were reacted and the molten mass was soaked at this temperature for 2 hours. This was done to remove any air trapped in the melt. The material was air quenched to room temperature by taking out the crucible from the furnace. Furnace cooling of the material was avoided because it resulted in partial crystallization. Black lumps of glistening substance were taken out from the crucible.

It was found by quartz emission spectrographic analysis that the silica pick-up in the material during the reaction was negligible.

X-RAY ANALYSIS

The lumps were crushed and ground to a fine powder. The powder was filled in a fine capillary required for X-ray diffraction. Diffraction pattern was taken with Mo K α radiation. The pattern showed no observable lines in it. This indicated the absence of any crystallization taking place during quenching and confirmed the vitreous nature of the material. The X-ray pattern is displayed in Fig. (2.1).

The glass lumps were then crushed and finely ground under distilled acetone using agate mortar and pestle. This was later wet milled in a porcelain jar using ceramic balls and acetone as the medium. After 12 hours of milling, the slurry was drained into a clean glass crystallizing dish. The slurry was dried free from acetone by heating in an electrical drying oven at 110°C for one hour. The dry powder was bottled and preserved for the preparation of paste. The particle size was found to be 1-2 μ , observed under optical microscope. Butanol and glycerine were used for dispersion.

PREPARATION OF VP GLASS PASTE



**FIG.2.1.X-RAY DIFFRACTION PATTERN
OF VP GLASS**

known as inks, paints and formulations. Generally, the pastes consist of four components; electrically active materials, a low softening glass, organic filler and solvents. Each of the components has a definite role to play. The glass acts as a permanent binder between the electrically active particles and substrate; the organic part controls the viscosity of the paste. These pastes have thixotropic properties.

In our case, the VP glass performs the twin role of the first two components.

Ethyl cellulose, butyl cellosolve and butyl carbitol acetate along with VP glass were used to prepare the paste.

A small quantity of VP glass powder was taken. Corresponding quantities of components of organic binder were calculated in the ratio 60:40 (glass:binder) for the preparation of paste. The organic binder itself was prepared by taking 10 parts of ethyl cellulose and 90 parts of the solvent mixture. The solvent mixture consisted 50:50 butyl carbitol acetate and butyl cellosolve.

EFFECT OF FLUIDITY OF THE PASTE ON SCREEN PRINTING

Fluidity of the paste depends on the extent of organic part which goes in its formulation. Pastes must exhibit certain amount of yield such that flow occurs under squeegee pressure, it should then stiffen and remain in position. Too much flow

little flow results in the retention of screen pattern on the prints.

Several formulations were studied and the results are presented below:

<u>Ratio of VP glass to organic binder (wt.%)</u>	<u>Effect on screen printing</u>
70:30	Loosely bound mixture, not possible to print.
65:35	Very thick paste, screen clogging, poor adhesion to the substrate.
60:40	Paint like in consistency, easy to print, good line definition, good adhesion to the substrate.
50:50	Very fluid, poor line defi- nition, smearing of the substrate with the paste.

In the light of the above observations, we selected a 60:40 ratio for formulations for our further work.

A typical formulation is as follows:

Vanadium phosphate glass	5.00 g.
Ethyl cellulose	0.33 g.
Butyl carbitol acetate	1.48 g.
Butyl cellosolve	1.48 g.

PREPARATION OF GOLD PASTE

A dried duPont's gold paste No: 7728 was suitably modified for our purpose.

A low softening glass, $\text{CdO}:\text{B}_2\text{O}_3.\text{Bi}_2\text{O}_3$ was prepared by melting the constituent oxides in a vitreous silica crucible at high temperatures ($\sim 800^\circ\text{C}$) in an electrical muffle furnace. The molten mass was fritted in distilled water. The glass was crushed to coarse powder under water. Later, it was ball milled to a very fine powder in a porcelain jar using ceramic balls and distilled water. After 24 hours of milling, the slurry was drained into a porcelain basin. This was dried in an electrically heated drying oven. The particle size of this glass powder was from 1 to 2μ as observed from an optical microscope.

Ten parts of this glass were added to 90 parts of the above mentioned gold paste and was well masticated using the required quantity of butyl carbitol acetate to get screen printable gold paste. This paste was used for providing electrodes.

PREPARATION OF STENCILS FOR SCREEN PRINTING ELECTRODES AND VP GLASS

[A] Stencil for electrodes

Silk bolting cloth (300 mesh) was made wet with water. This wet cloth was stretched and fixed on to a $1\frac{1}{2}$ " thick wooden frame of 10 cm. x 20 cm. The cloth remained very taut. Orthogonality of the mesh was maintained as much as possible

while fixing the cloth to the frame. The screen was then dried. Glass sheet backed adhesive film was taken. A rectangular portion of 2 mm x 20 mm was cutout from the centre of the adhesive film using a sharp blade. The cut portion was lifted up with a thin chisel edge of a stainless steel rod and removed. The adhesive film was carefully peeled off from the glass plate and transferred on to the screen. The frame was placed on a level place and the adhesive was well rubbed from inside to ensure perfect adherence of the adhesive film to the screen. Absence of any air trapped between the adhesive film and the screen was ensured. This stencil would deposit print of 2 mm x 20 mm size on the substrate.

[B] Stencil for VP glass

Essentially, the procedure was same as in (A) for making this stencil. Here the silk bolting cloth was 180 mesh and a circular portion (3 mm dia.) was cutout from the adhesive film. Other details were same as in (A).

These stencils are shown in Figures 2.2(A), 2.2(B).

PRINTING BOARD

A small 30 cm x 45 cm formica top printing board was used. It has arrangement to hold the stencil screen frame firmly in position by a C-clamp. A square slot is provided on the board for holding the substrate firmly in position. The printing board is shown in Figure (2.3).

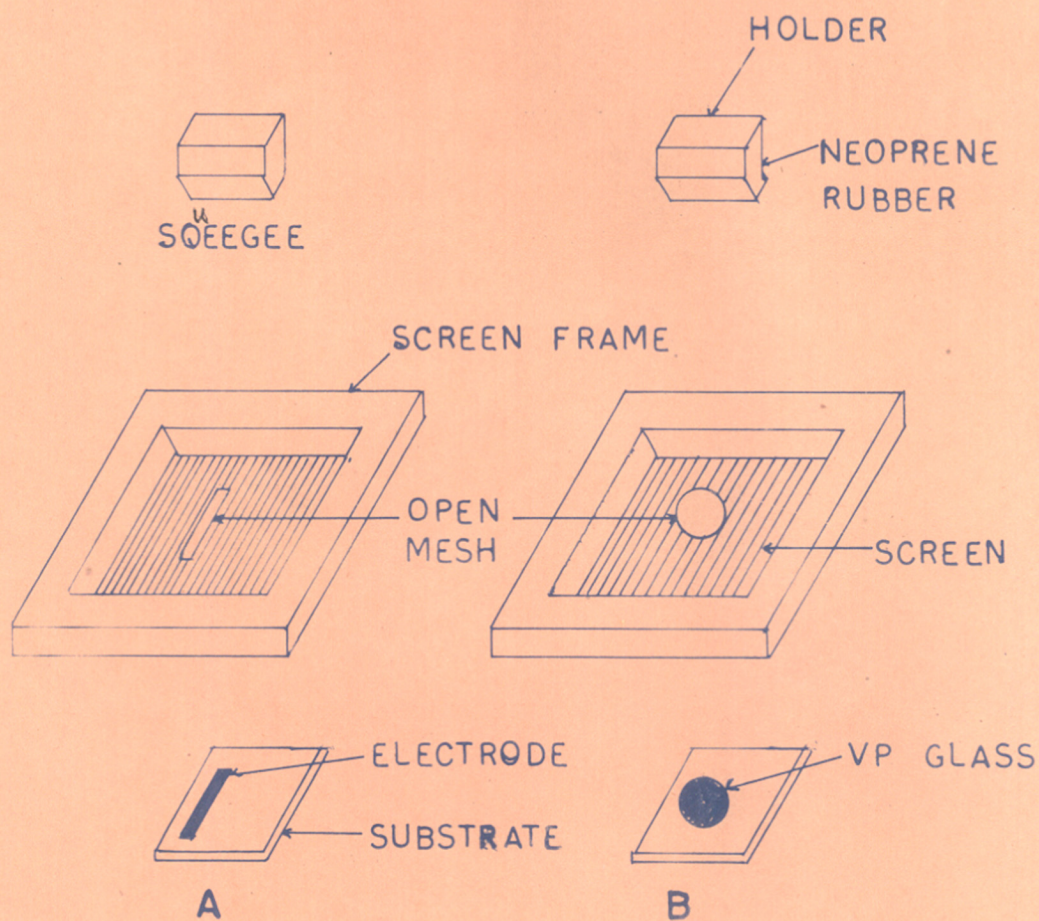
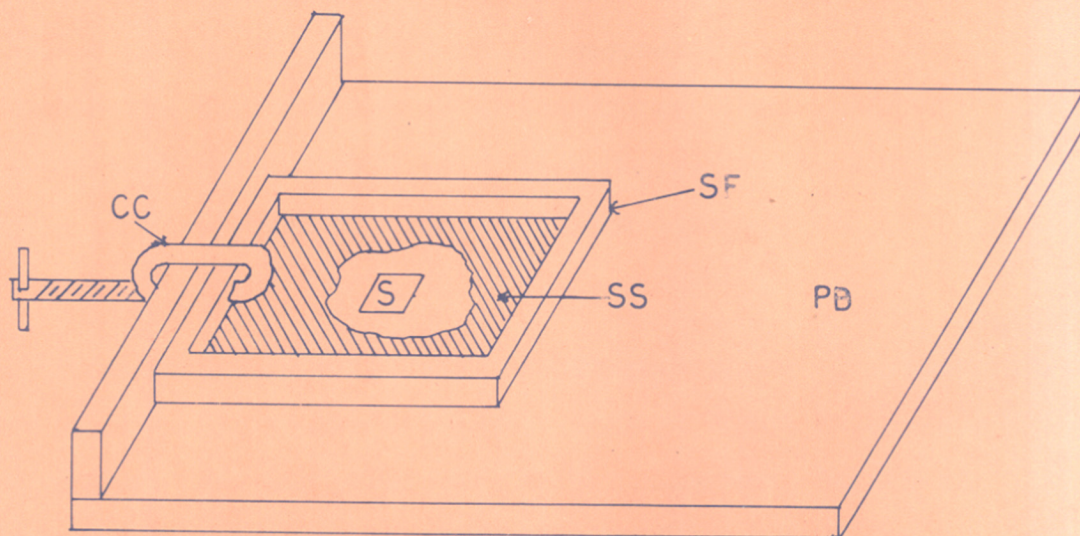


FIG.2.2 SCHEMATIC SCREEN
PRINTING PROCESS



CC	C CLAMP
S	SUBSTRATE
SF	SCREEN FRAME
SS	SCREEN STENCIL
PB	PRINTING BACE

FIG.2.3 PRINTING BOARD

S Q U E E G E E

The squeegee material should be compatible with the solvents used in thick film process. It should not swell, distort or wear with use. Generally neoprene, polyurethane or "viton" are used for making the squeegees. The hardness (normally 50-90 durometer), the attack angle, the pressure we apply and the speed of movement of the squeegee are important.

We have used a rectangular neoprene piece of 2 mm x 5 cm with a square cut edge. This is fixed in a brass holder. Certain parameters in printing were not fixed as it was done manually. The squeegee is depicted in the Figure (2.2).

SUBSTRATE

The higher firing temperatures necessitate the use of ceramic materials for substrates. 96% Alumina has been very widely used in thick film industry. This material has all the required properties. This has coefficient of thermal expansion equal to $6.0-8.0 \times 10^{-6}$ in/(in.)(°C). We have also used 96% alumina substrates (1"x1"x0.002") obtained from M/s. Electronic Slicing and Dicing, Inc., USA, with the following specifications:

Material	: 96% Al_2O_3 as fired
Length and width tol:	$\pm 1\%$ NLT ± 0.005 in.
Thickness tol.	: $\pm 12\%$ NLT ± 0.0015 in.
Camber	: 0.004 in./in.

EXPERIMENTAL TECHNIQUES

Preparation of the sample

Alumina substrate was firmly positioned on the base of the printing board, Figure (2.3). The screen stencil Figure (2.2A) was fixed to the board with the C-clamp such that the rectangular stencil was positioned on the substrate.

Deposition of bottom electrode

Gold paste was deposited on the stencil. The squeegee was brought into position to have a physical contact with the stencil. As the squeegee was advanced, the paste was pressed through the open mesh and got deposited on the substrate. As the squeegee blade was passed, the tension in the screen snapped it back separating from the substrate. A brown rectangular print was deposited on the substrate. The print was dried at 150°C/15 minutes under infrared lamp. The solvent was removed and volume shrinkage took place. The print was then fired at 800°C for 10 minutes. The organic binder was burnt off and the glass particles fused and formed a vitreous bond between the gold particles and the substrate. This formed the bottom electrode (2 mm x 20 mm) of the Au-Glass-Au sandwich. The resistance of the print was $< 0.05 \Omega/\text{mm}$.

Printing of VP glass paste

The substrate with bottom electrode was positioned on the printing board. The second stencil (2.2B) was clamped to the board. Sequential operations for getting the VP glass print

were same as in the case of bottom electrode. The circular print of VP glass was on one end of the bottom electrode. The print was dried as usual and fired in the furnace at $510^{\circ} \pm 10^{\circ}\text{C}$ for 2-3 minutes. The print was air quenched by removing the substrate from the furnace on to a metal plate. The resulting print was black with a glassy smooth surface.

Deposition of top electrode

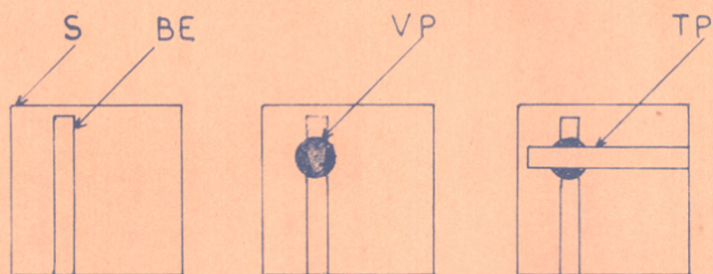
(i) By screen printing : The sequence of operations for getting top electrode was the same as in the case of bottom electrode except that the stencil was turned through 90° . The top print was dried as usual and fired at 450°C for 10 minutes this time.

The sequence of the above printing process is shown in Fig. (2.4). Also the Fig. (2.5) gives an idea how the printing operation is actually carried out.

(ii) By vacuum evaporation : We found no difference between the thick film method and thin film method as far as the electrodes were concerned.

Vacuum deposition unit

An all glass vacuum unit (Fig. 2.6) was used for the purpose. An oil rotary vacuum pump was used as the backing pump. This was connected to a drying tube containing P_2O_5 and then to a cold trap. This was followed by a mercury diffusion



S — SUBSTRATE

BE — BOTTOM ELECTRODE

VP — VP GLASS

TP — TOP ELECTRODE

FIG. 2.4 PREPARATION OF SANDWICH
SAMPLES

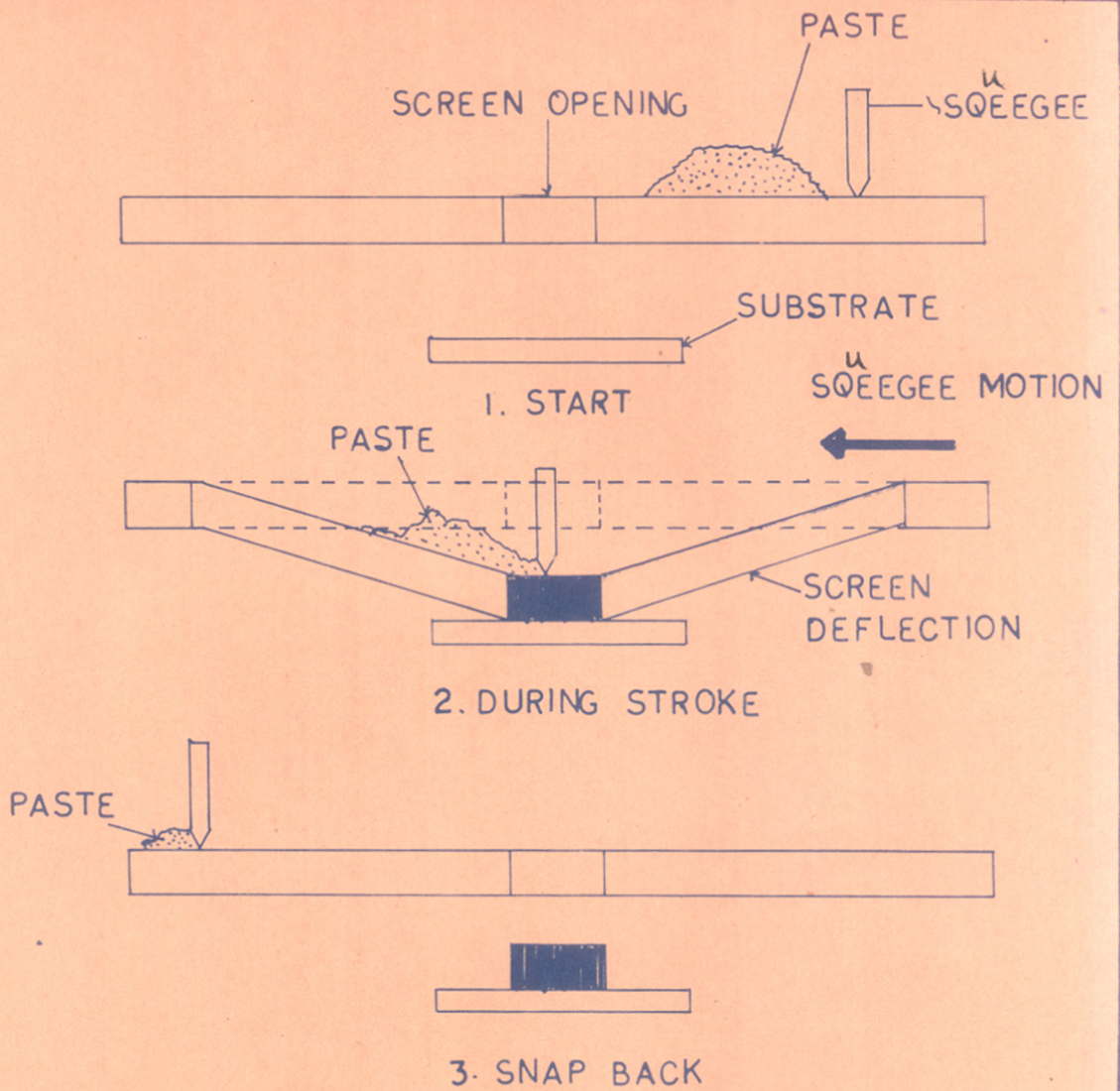


FIG.2.5 SCREEN PRINTING CYCLE

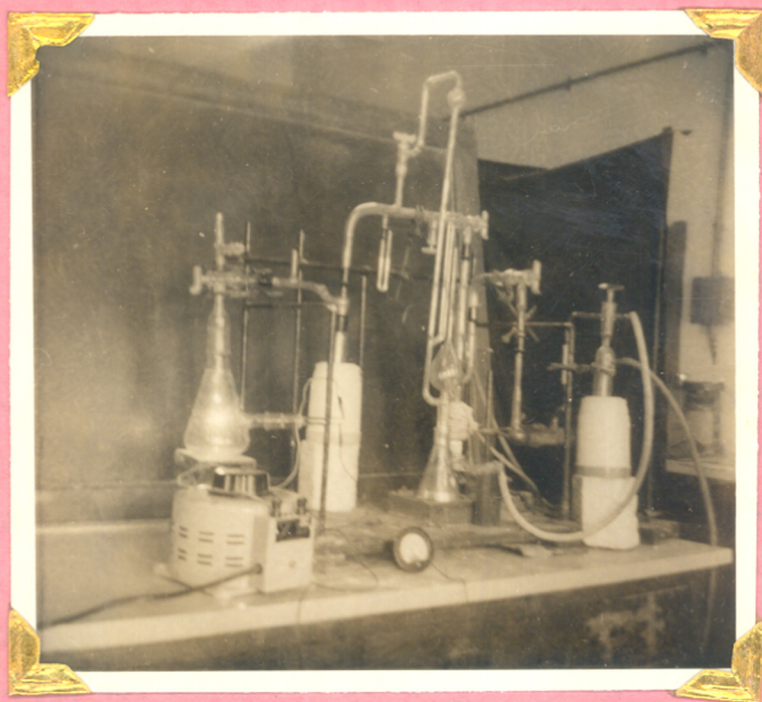


FIG.2.6. VACUUM DEPOSITION UNIT

pump. Pressure measurements were done with a McLeod gauge. A deposition chamber was connected to this assembly.

The bottom electrode and VP glass print were suitably masked with mica having a rectangular slit of 2 mm x 20 mm, perpendicular to the bottom electrode.

This was placed at the bottom of the deposition chamber. A tungsten filament was connected to two copper electrodes coming through a B-29 female joint. This joint fits on to the B-29 male joint at the side of the chamber. The copper electrodes were sealed with araldite. The distance between the masked substrate and the filament was 5-6 cms. Either gold or aluminium wires, in the form of loops, were hung on the filament. The deposition chamber was connected to the vacuum unit. When a vacuum of the order of 10^{-6} torr was obtained, the tungsten filament was heated by passing current slowly till the metal melted in the filament. On increasing current thereafter, metal evaporated and deposited on the substrate.

After taking necessary precautions, the vacuum was released and the deposition chamber was removed. The sample was taken out.

DTA/DTG/TG

Thermogravimetric analysis is a good experimental tool to find out the thermal effects and oxidation-reduction phenomenon in the sample material.

Thermograms were taken both for the powder and paste of the vanadium phosphate glass. This was done to see whether there would be reduction of V_2O_5 to VO_2 taking place in the reducing atmosphere created by the pyrolysis of the organic binder used for making the paste.

Derivatograph type OD-102 made by MOM, Budapest, was used for DTA/DTG/TG measurements. This measures the change in weight (TG), the rate of change of weight (DTG) and the change in heat content (DTA) of the sample material simultaneously, while the sample is being heated at a particular uniform rate. Same quantities (200 mg.) of each of the sample and the reference material (Al_2O_3) were taken. The furnace chamber was evacuated by a water suction pump. The heating rate was adjusted at $10^\circ C/minute$.

The DTG-galvanometer measured the current induced by the coil suspended from the analytical balance beam and moving in magnetic field.

The DTA-galvanometer measured the difference of emfs between two thermocouples (chromel-alumel) one from the inert material and the other from the sample under study.

The T-galvanometer measured the temperature of the sample alone.

D. C. conductivity

Two probe D. C. method was used for the measurements. In order to have ohmic contacts, several materials like platinum paste, silver paste, palladium paste, SnO_2 , gold paste, were tried. Gold was found to give ohmic contacts. Bidirectional measurements were carried out and their average taken to avoid any thermoelectric contribution to the measured signal.

Majority of the workers^{7,86,87} have used vacuum evaporated gold contacts for the vanadium phosphate glasses.

Experimental set-up

Resin coated copper wires (28 SWG) were soldered to the two electrodes of the Au-VP glass-Au sandwich structure. The junction of the copper constantan thermocouple was fixed very near to the sample. The substrate was mounted on a teflon block. The block was introduced in a glass envelop GL Fig.(2.8). The lead wires and thermocouple wires were taken out through the holes provided to the glass cap. They were sealed by putting araldite. The cold junction was introduced in kerosene oil in a glass tube which was kept cool in ice. The glass envelop was connected to a rotary vacuum pump. A vacustat was used to measure the pressure in the system. A ground glass joint was provided to facilitate easy handling and mounting of the samples.

The glass assembly was introduced in an electrical wire wound tubular furnace. A temperature controller and a variable transformer were used to maintain the required temperature around the sample.

A schematic diagram for conductivity measurements is shown in Fig. (2.7).

Low voltage measurements were carried out to avoid possible joule heating. A potentiometer was used as a potential source with voltage increments of 0.1V upto 1.7 volts. Philips (GM6020) D.C. Microvoltmeter was used to measure voltage drop across the standard resistor. The current through the sample was calculated from this potential drop. Voltage drop across the sample was measured by a VTVM of Ruttonsha Simpson (Model 221-1). Pye potentiometer was used for measuring the temperature in terms of thermo emf.

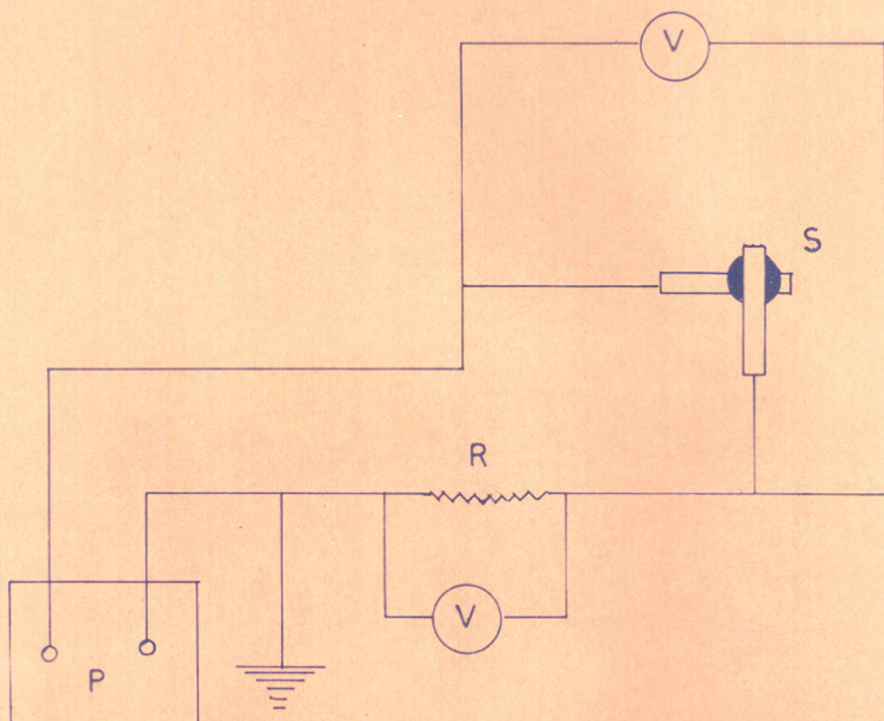
The resistance of the sample was calculated at different temperatures from (300°K to 395°K) using the above set up. For low temperature measurements (256°K to 300°K), the sample holder was introduced into a Dewar flask containing cooling mixture. Further low temperature measurements were not carried out since the resistance values were very high.

Thermo emf measurements

When two ends of a conductor are kept at different temperatures, an emf proportional to temperature difference is established. The thermo emf per degree is called thermoelectric power or Seebeck coefficient.

Sample preparation

Two screen stencils were used; one to print 3 sq. mm. electrodes with an interelectrode distance of 3 mm. and another



S—SAMPLE
 R—STANDARD RESISTOR
 P—POWER SUPPLY
 V—VTVM

FIG.2.7 SCHEMATIC CIRCUIT DIAGRAM
 FOR
 σ AND I-V CHARACTERISTICS
 MEASUREMENTS

to deposit a rectangular print of 1 mm. wide x 6 mm. long on these electrodes.

Alumina substrate was fixed on the printing board. The first stencil was fixed over the substrate. Gold paste was screen printed on to the substrate through the stencil. Drying and firing of these prints were carried as described earlier.

Second stencil was then fixed to the printing board. A rectangular print of 1 mm. x 6 mm. of VP glass paste was deposited on the electrodes with an overlap of 1 mm. x ~~1~~⁵ mm. on each of them. Again, drying and firing of the sample were same as before.

Description of sample holder

The assembly unit is shown in the Fig. (2.8). Two mica pieces (15 mm. x 20 mm.) were fixed in the grooves of two rectangular teflon pieces. There was a 3 mm. gap between the mica pieces. This gap was provided to avoid the heat transfer by conduction through mica. The substrate on which the sample was printed, was placed on the mica pieces such that the sample was at right angles to the gap. On one of the electrodes of the sample a tin oxide coated glass microheater (50- Ω) was seated by cutting out small portions on the teflon pieces. Two phosphor bronze strips were fixed to the teflon pieces. The other ends were bent to have spring action to hold the two ends of the heater on which air drying silver paste had been applied earlier. Two resin coated copper wires were soldered to the

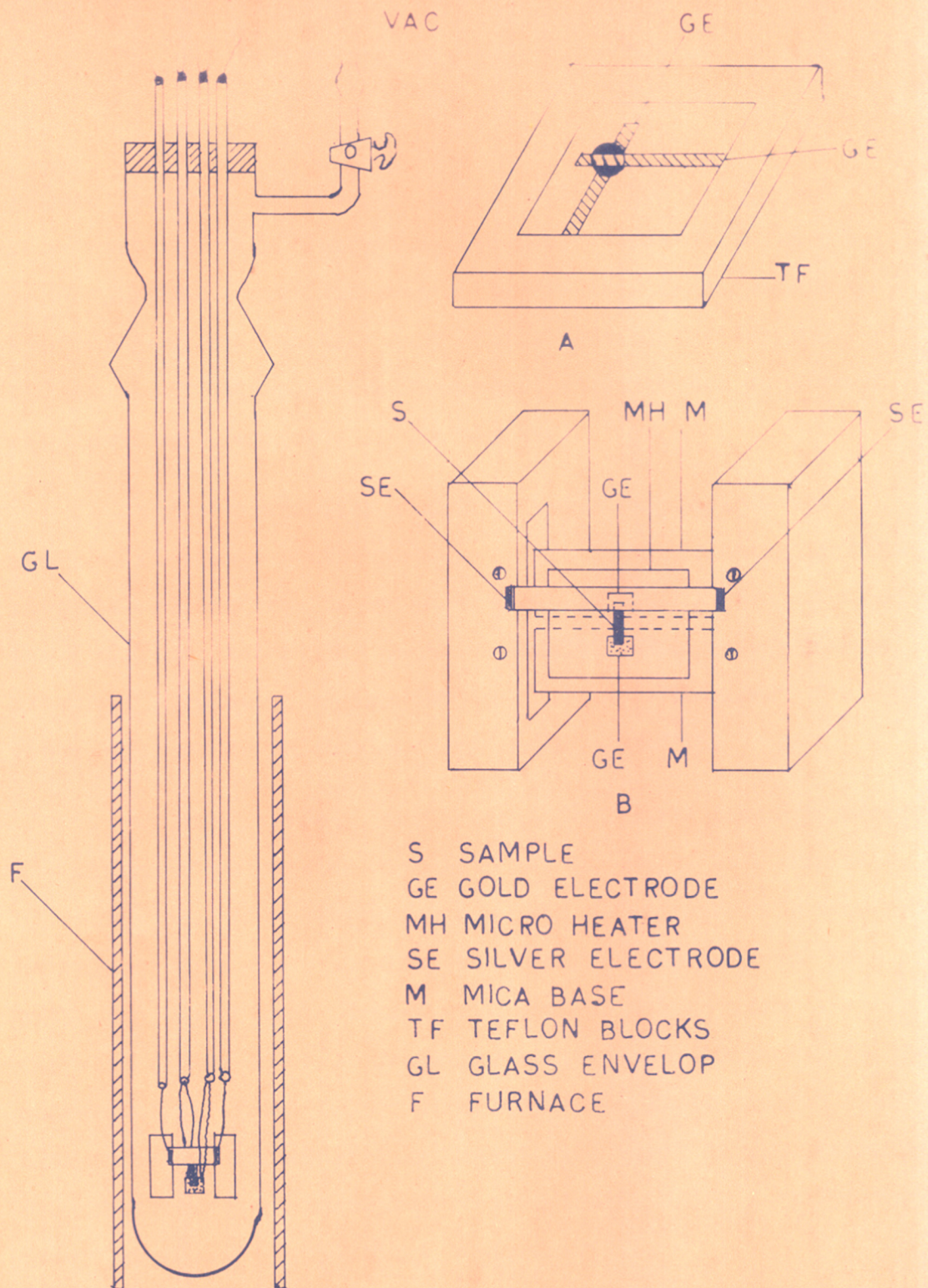


FIG. 2.8 SAMPLE HOLDER FOR
THERMO EMF MEASUREMENTS

eyelets fixed to the phosphor bronze strips for the supply of current from a D. C. source. Two copper-constantan thermocouple junctions were soldered on to the gold electrodes with the junction tips touching each of the ends of the sample. The two copper wires of the thermocouples were used to measure the thermo emf generated in the sample.

The most familiar source of noise external to the specimen is electrostatic pick-up. This is unavoidable in high impedance circuitry. In order to minimize this source of noise, the measurement circuitry is to be shielded from stray sources of charge by placing the system in a copper enclosure. The lead wires are also to be shielded and ground properly.

In our assembly, due precautions were taken to avoid any pickups from outside signals. All the wires were shielded by using 2 mm. dia. copper tubing. The teflon sample holder was introduced in a glass envelop which in turn was inserted in a tight fit copper cap. Common mode pick-up due to stray electromagnetic fields and high frequency pick-up are eliminated in the microvoltmeter front filter circuitry. The whole assembly was introduced in an electrically heated wire wound tubular furnace. The temperature was accurately controlled by using a variable transformer and a temperature controller.

The copper tubes were taken out through the joint. The interspace was sealed by filling with araldite. The wires were sealed in the copper tubes with araldite. The lead wires and the

thermocouple wires were soldered to specially made terminals fixed to a panel. The panel was encased in copper sheet.

A D. C. power supply was connected to the microheater for heating one end of the sample. Philips D.C. (PP 9064) microvoltmeter was used to measure the thermo emf as well as the temperatures of the two ends of the sample.

All the measurements were carried out after baking the sample at $120^{\circ}\text{C}/2$ hours under vacuum of the order of 10^{-2} torr.

The circuit diagram is shown in Fig. (2.9).

I-V characteristics

[a] Au-VP glass-Au

These sandwich structures were prepared as described earlier.

[b] Au-VP glass-Al

The bottom gold electrode followed by the VP glass prints were obtained as described earlier. After suitable masking, sample was introduced in the deposition chamber. Aluminium wire was taken in the tungsten filament. Flash evaporation was done to get an aluminium deposit of 2 mm. x 20 mm. on the VP glass print and at right angles to the first electrode.

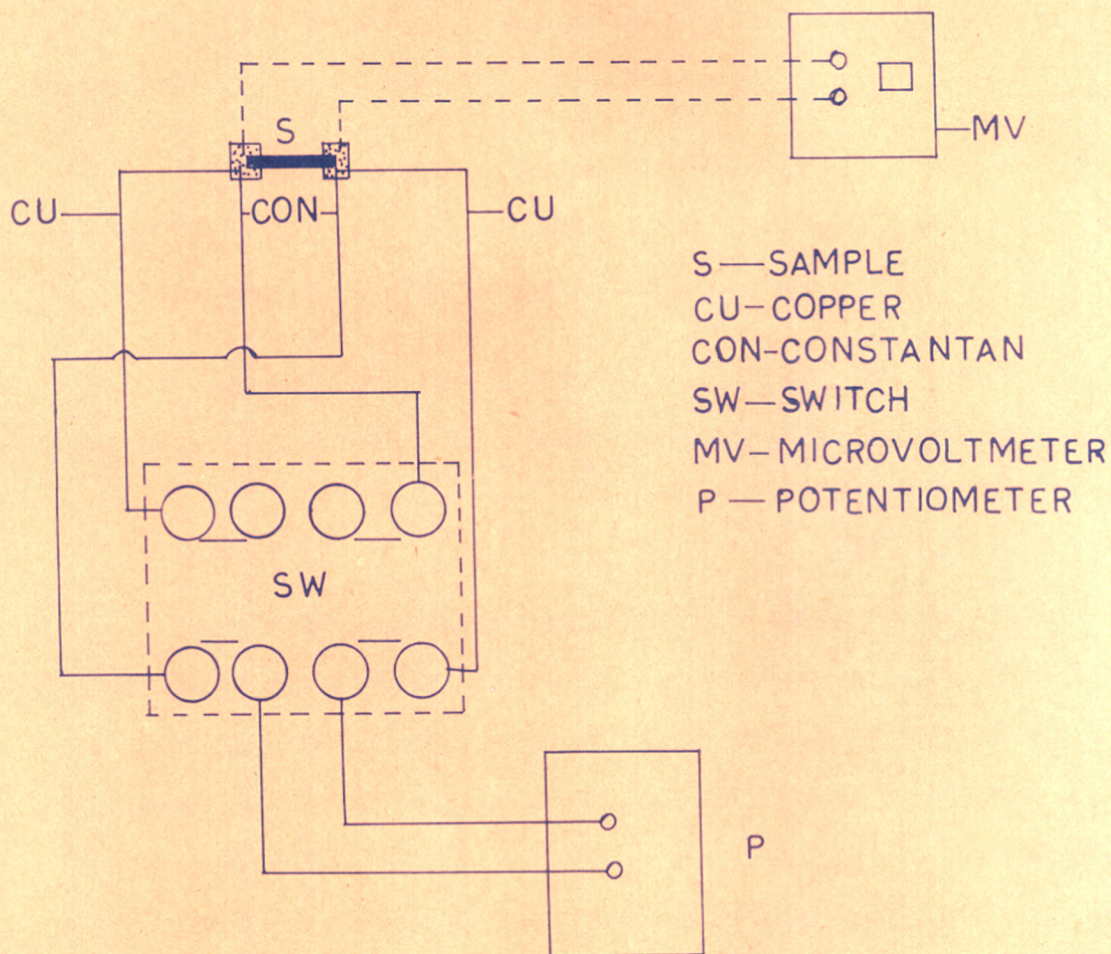


FIG.2.9 CIRCUIT DIAGRAM FOR
THERMOEMF MEASUREMENTS.

[c] Al-VP glass-Al

Alumina substrate was masked by mica having a slit of 2 mm. x 20 mm. Aluminium was flash evaporated following the procedure mentioned earlier.

VP glass paste was screen printed on this electrode. Rest of the electrode was covered by gold paste. After drying, the sample was fired following the same procedure.

Finally, the top aluminium electrode was vacuum deposited on the sample at right angles to the bottom electrode.

Contacts

For studying the current-voltage characteristics of the metal-VP glass-metal sandwich structures, press contacts were used. A thin, dry aluminium foil was placed on the metal electrodes. Crocodile pins with flat jaws were used for pressure contacts. Resin coated copper lead wires were soldered to the pins. The assembly was the same which was used for the D. C. conductivity measurements Fig. 2.8A

After evacuating the sample holder, the sample was baked at $120^{\circ}\text{C}/2$ hours under vacuum of the order of 10^{-2} torr.

Experimental set-up

A schematic diagram is shown in the Fig. (2.7).

Stabilized D. C. power supply (Beltronix) 0-50V, 0-2A was used as a potential source. D. C. microvoltmeter PP9064 measured the voltage drop across the standard resistor. Voltage

drop across the sample was measured by a VTVM (Ruthonsha Simpson) in both directions. This was done to correct for any error due to stray thermo emfs. Applied voltage polarity was changed and the voltage increase/decrease was done in steps of 2V.

The current through the sample was calculated from the voltage drop across the standard resistor.

RESULTS AND DISCUSSION

DTA/DTG/TG

The thermal characteristics of VP glass and VP glass paste, as revealed by DTA, DTG and TG curves, are represented in Figures 3.1 and 3.2.

In both the cases, DTA curve shows a sharp endothermic peak at 505°C indicating the melting transition of the glass at this temperature. Also, there are two small exothermic peaks at 335°C and 385°C . There is a weight loss shown on the TG curve corresponding to the first exothermic peak. There is hardly any change in weight over the previous situation corresponding to the second exothermic peak. These are the common features between the two figures.

VP glass

The DTG curve indicates a peak between 335°C and 425°C which corresponds to the two small successive exothermic peaks on DTA curve.

The loss in weight starts at 50°C , is gradual in the beginning, has a sharp jerk at 160°C , reaches maximum at 290°C and remains constant upto 350°C .

The gradual loss is explained by associating it with particle size of the sample. It is reported that when the particle size is very small, it is observed that there would be a continuous loss from 50°C onwards, whereas when a massive material is taken, it is observed that little mass-loss occurred until a higher temperature is reached.

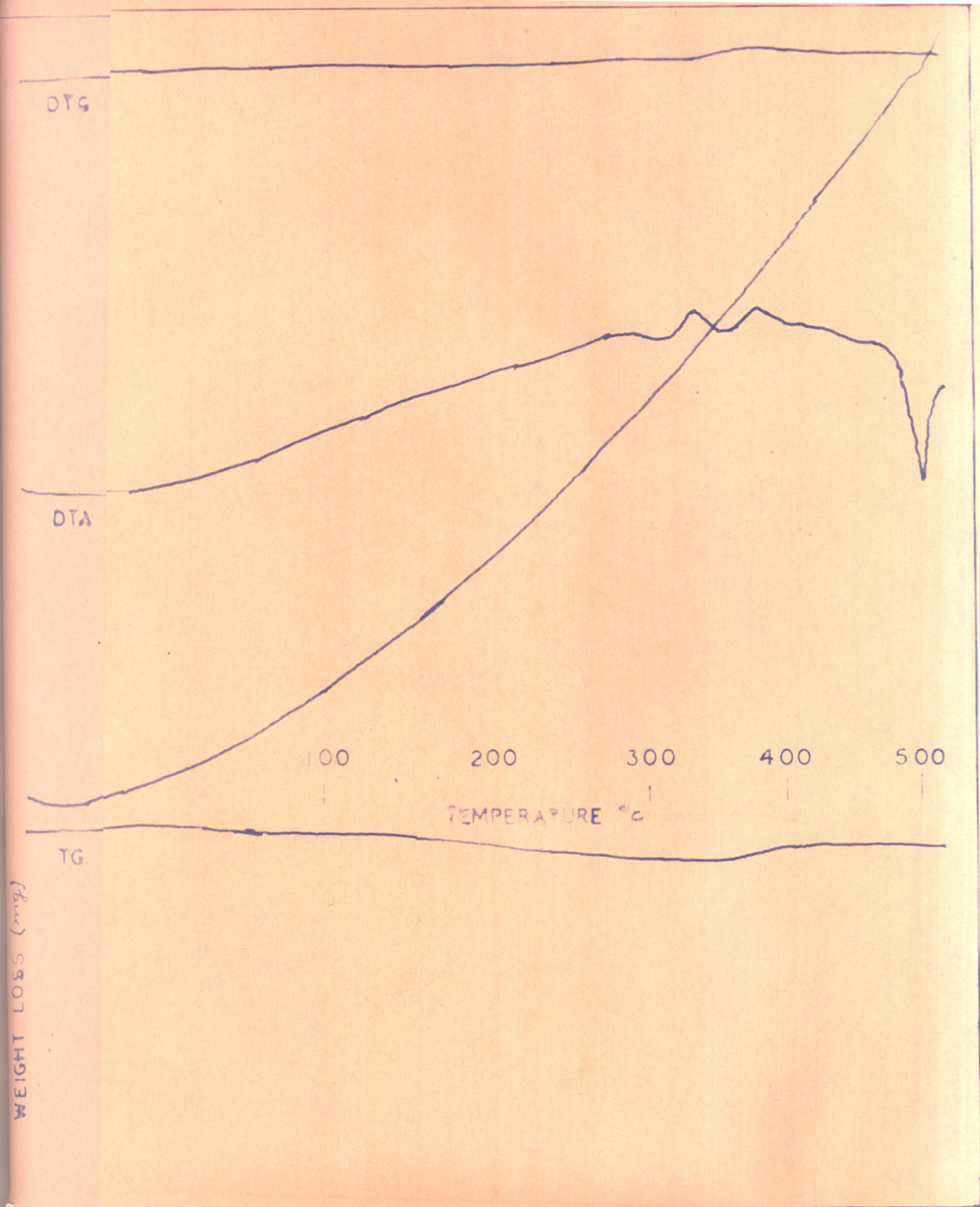


FIG.3.1 DTG DTA AND TG OF VP GLASS

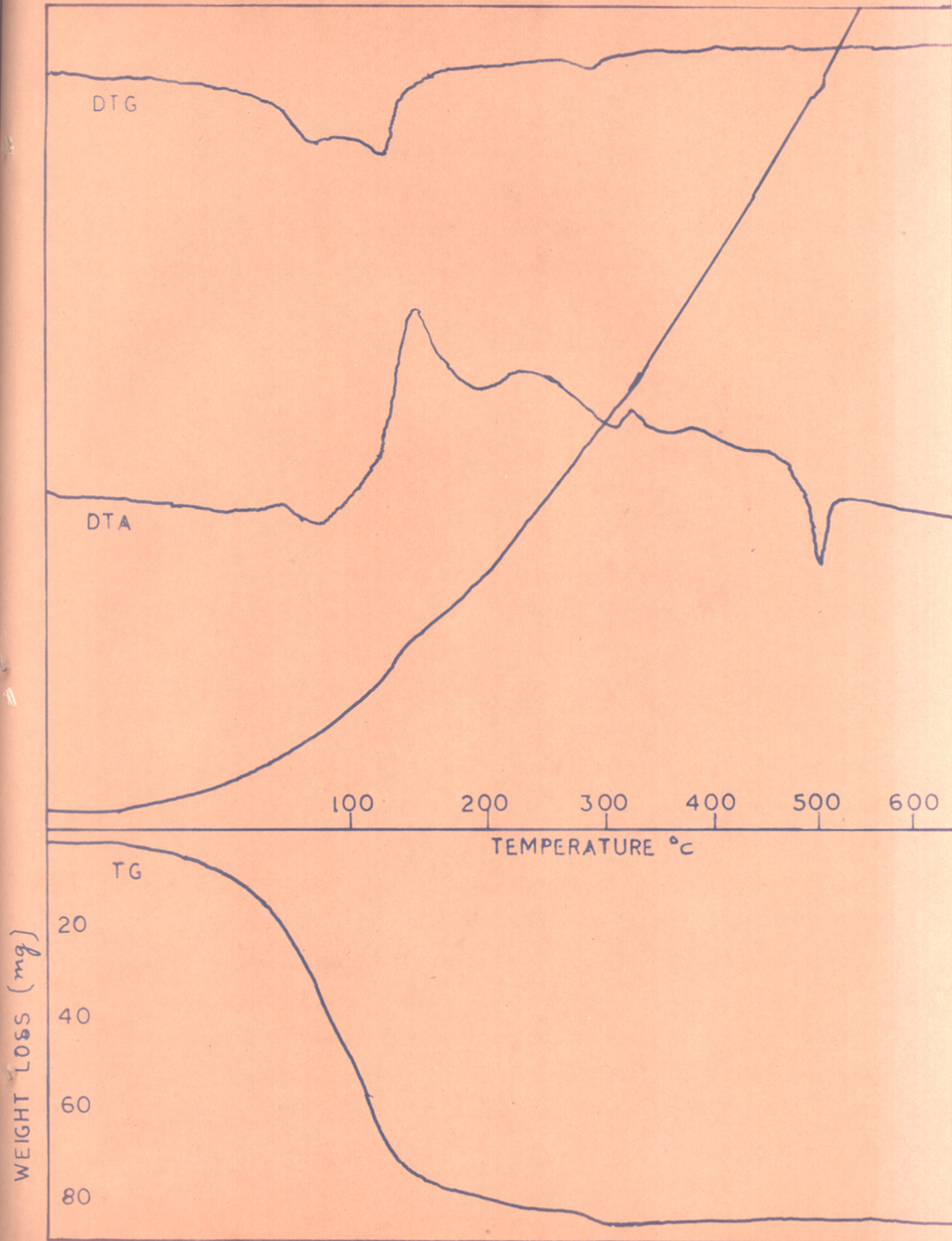


FIG 3.2 DTG, DTA AND TG CURVES

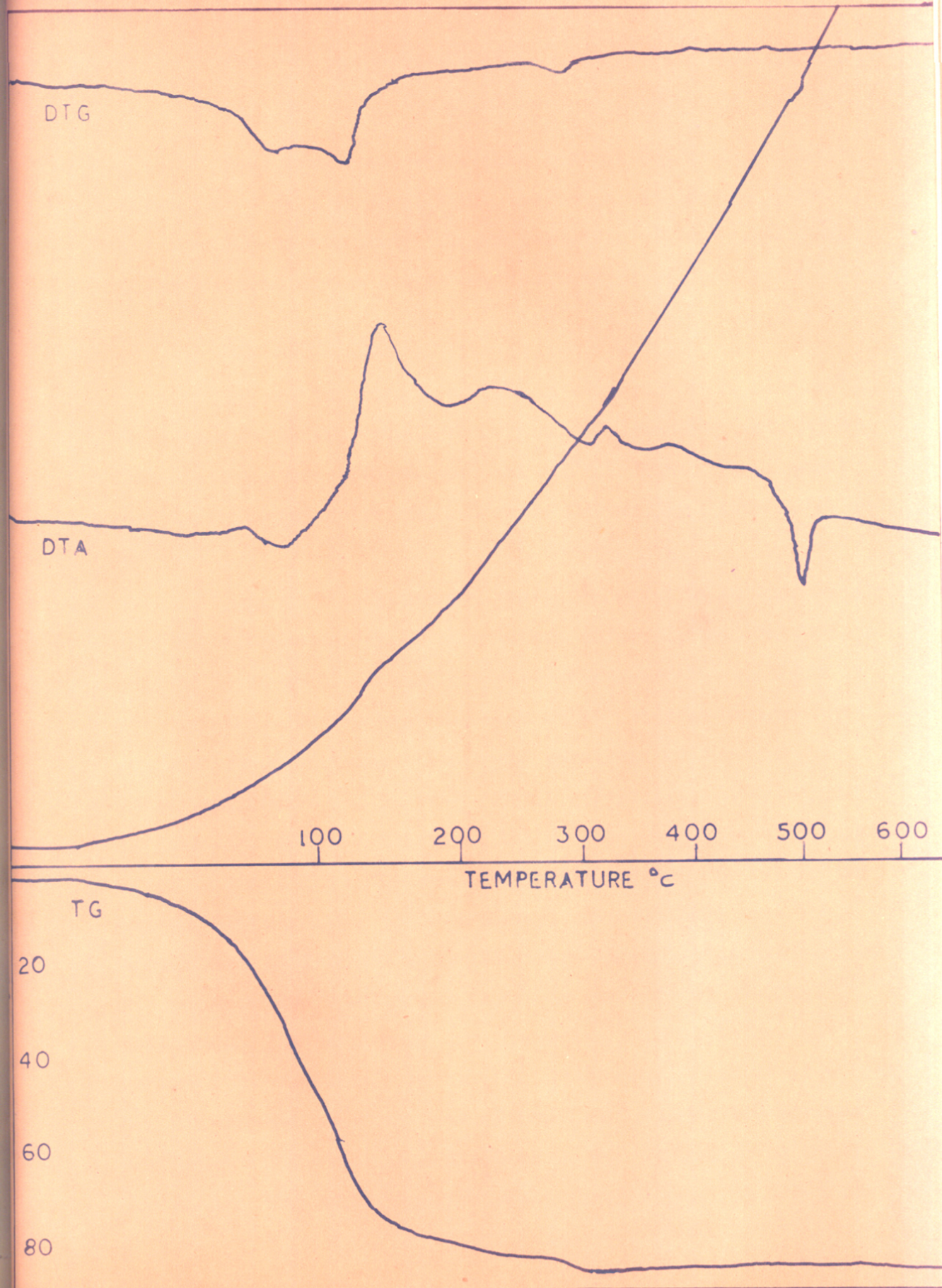


FIG. 3.2 DTG, DTA AND TG CURVES

From TG curves, the weight loss at 335°C is about 4% followed by a gain of about 1.0%, leaving a net loss of 3.0%. This loss may be attributed to the formation of VO_2 . The second exothermic peak may be due to crystallization of this oxide.

VP glass paste

TG : The loss in weight is at a slow rate upto 50°C . It is then very fast upto 150°C . Then it slows down upto 300°C . There is a plateau between 300° and 400°C . Thereafter a small gain is indicated which falls back to the original loss level at 600°C .

DTA : A broad narrow trough followed by an endothermic peak indicates evaporation of moisture and solvents. There is a loss of 5% at 45°C . A small overlap of evaporation of these is not excluded. The endothermic peak at 85°C may be assigned to evaporation of solvents. Immediate pyrolysis of the solvents (butyl cellosolve, B. P. 171°C ; butyl carbitol acetate, B.P. 247°C) is indicated by the exotherm at 155°C . The weight loss at this stage is about 37% which accounts to the solvent content of the paste. Corresponding to this thermal effect, there is a large trough from 60°C to 165°C on DTG. There is an exothermic peak on DTA curve at 240°C which may be due to the burning of ethyl cellulose. The burning of the binder has started before the solvents are completely burnt off. This overlap can be seen from the DTA curve. A weight loss of about 4% is indicated between 155°C and 240°C which is equivalent to the percentage of binder in the paste. The two exothermic peaks at 335°C and 385°C may be

assigned to the formation and crystallization of VO_2 . The glass starts softening at 410°C and finally melts at 505°C . The endotherm on DTA curve indicates this transition.

Thus, from the thermal analysis of vanadium phosphate glass and paste, we can infer several facts. The total solvent and binder loss as indicated by the TG curve corresponds to the quantities we have taken. Organic part completely burns off before the sample reaches 290°C .

The pyrolysis of the organic part has apparently not affected the nature of chemical transitions taking place in the glass in the subsequent stages of heating. The VO_2 formation is seen even in the VP glass without the organic part. This analysis also helped us in fixing the temperature at which the glass prints are to be fired to get a good glaze in sample preparation.

The weight loss as indicated by TG and exothermic peaks at 335°C and 385°C substantiate qualitatively the formation and crystallization of VO_2 . This transition has been reported to be responsible for threshold switching taking place when voltage is applied across the sample.

D. C. CONDUCTIVITY

In the measurement of electrical conductivity, the electrical contacts must not impede the flow of charge carriers. There should not be any air gap between the electrode and the sample. Following are the conditions for ideal contacts:

1. Electrodes should not introduce resistance to the flow of current.
2. Variations in applied voltage and temperature should not have any deleterious effects in the electrode material.
3. Compatability between the sample and electrode material.

An ohmic contact ($dI/dV = \text{constant}$) is essential for the electrical conductivity measurements. The difference in work functions between the metal contact and the semiconductor material results in non-ohmic contacts. This difference is equal to energy barrier. Problems associated with barrier layers can be eliminated by having pressure contacts and right selection of electrode material. In our case, air gaps between the contact and the sample have less chance to occur since the material deposited is melted and air quenched.

Regarding the selection of right type of electrode material, several metal pastes and SnO_2 were tried. Pd, Pt, Ag and Au were among the pastes tried. Except Au paste, others were not suitable. The VP glass was not wetting the electrodes after firing and air quenching with these contacts. Gold electrodes, both by screen printing and vacuum evaporation, were found to give ohmic contact.

The voltage drop across a standard resistance was used to calculate the circuit current. Using this value of current and potential drop across the sample, resistance of the sample was calculated from the Ohm's law $I = V/R$ where I = current, V = voltage

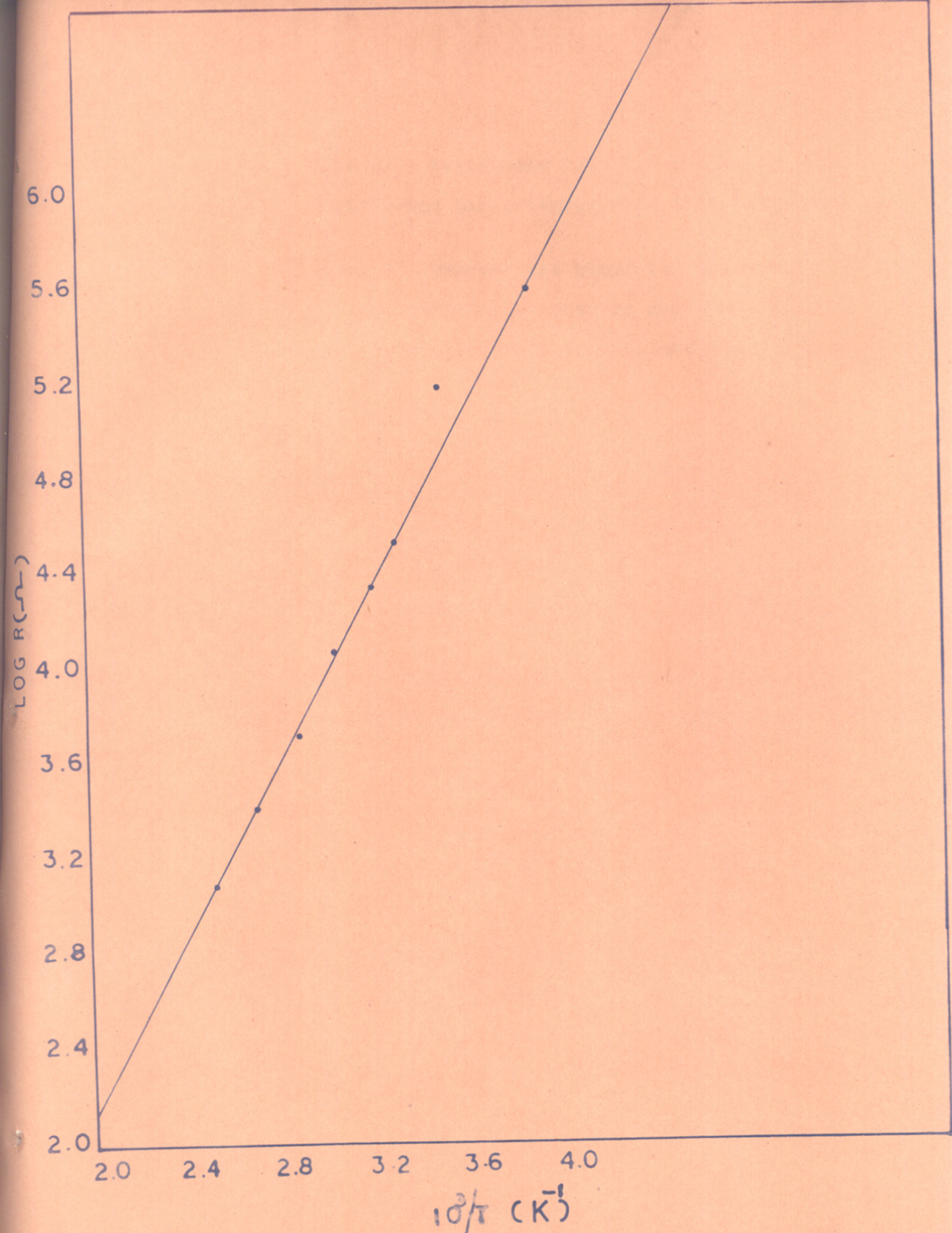


FIG.3-3 TEMPERATURE DEPENDENCE
OF RESISTANCE

and R = resistance. Resistance value of the sample was calculated at different temperatures from 256° to 395°K .

The $\log R$ - temperature graph for the sample ($70 \text{ V}_2\text{O}_5 : 30 \text{ P}_2\text{O}_5$) studied is shown in the Figure (3.3). The resistivity-temperature relation follows the equation

$$\rho = \rho_0 \exp E/KT$$

The activation energy is calculated from

$$E = 0.1987 \times 10^{-3} \frac{\Delta \log_{10} R}{\Delta(1/T)} \text{ eV.}$$

For our sample, the calculated figure was 0.38 eV .

The following table gives the activation energy values for various VP glasses reported in literature.

Table

<u>No.</u>	<u>Sample</u>	<u>Activation energy, eV</u>	<u>Geometry of the sample</u>	<u>Reference</u>
1.	$70 \text{ V}_2\text{O}_5 : 30 \text{ P}_2\text{O}_5$	0.38	Pellet	55
2.	$70 \text{ V}_2\text{O}_5 : 30 \text{ P}_2\text{O}_5$	0.34	"	59
3.	$\text{V}_2\text{O}_5 : \text{P}_2\text{O}_5$	0.35	"	66
4.	$70 \text{ V}_2\text{O}_5 : 30 \text{ P}_2\text{O}_5$	0.38	Thick film	Present work.
5.	$80 \text{ V}_2\text{O}_5 : 20 \text{ P}_2\text{O}_5$	0.37	Pellet	7
6.	$62 \text{ V}_2\text{O}_5 : 38 \text{ P}_2\text{O}_5$	0.40	"	84
7.	$65 \text{ V}_2\text{O}_5 : 35 \text{ P}_2\text{O}_5$	0.38	"	84
8.	$73 \text{ V}_2\text{O}_5 : 37 \text{ P}_2\text{O}_5$	0.38	"	84

The resistance of the sample at 300°K and 400°K is 38 K- Ω and 1 K- Ω . The temperature coefficient of resistance is calculated from

$$\text{T.C.R.} = 1/R \frac{dR}{dT}$$

which is equal to $\sim -4\%$ per degree at 300°K. There is a large variation of resistance with temperature. This value indicates the possibility of using the material for thermistor application. Conductivity measurements are carried out for the first time on samples of VP glass made by the thick film method.

THERMO EMF

Thermo emf was measured when the two ends of the sample were maintained at different temperatures. Temperature difference was varied from 0.4°C to 16°C between the ends. The thermoelectric power (Seebeck coeff.) was calculated from

$$S = \frac{P.D.}{\Delta T} \quad \mu\text{V/degree.}$$

It varied from +20 μV to -28 $\mu\text{V}/^\circ\text{K}$ in the temperature range from 300°K to 425°K. The results are shown in the Figure (3-4).

At room temperature the Seebeck coefficient is small (20 $\mu\text{V}/^\circ\text{K}$) and positive (i.e. the cold junction is positive). It decreases with the increasing temperature, changes sign at about 60°C and becomes negative at higher temperatures.

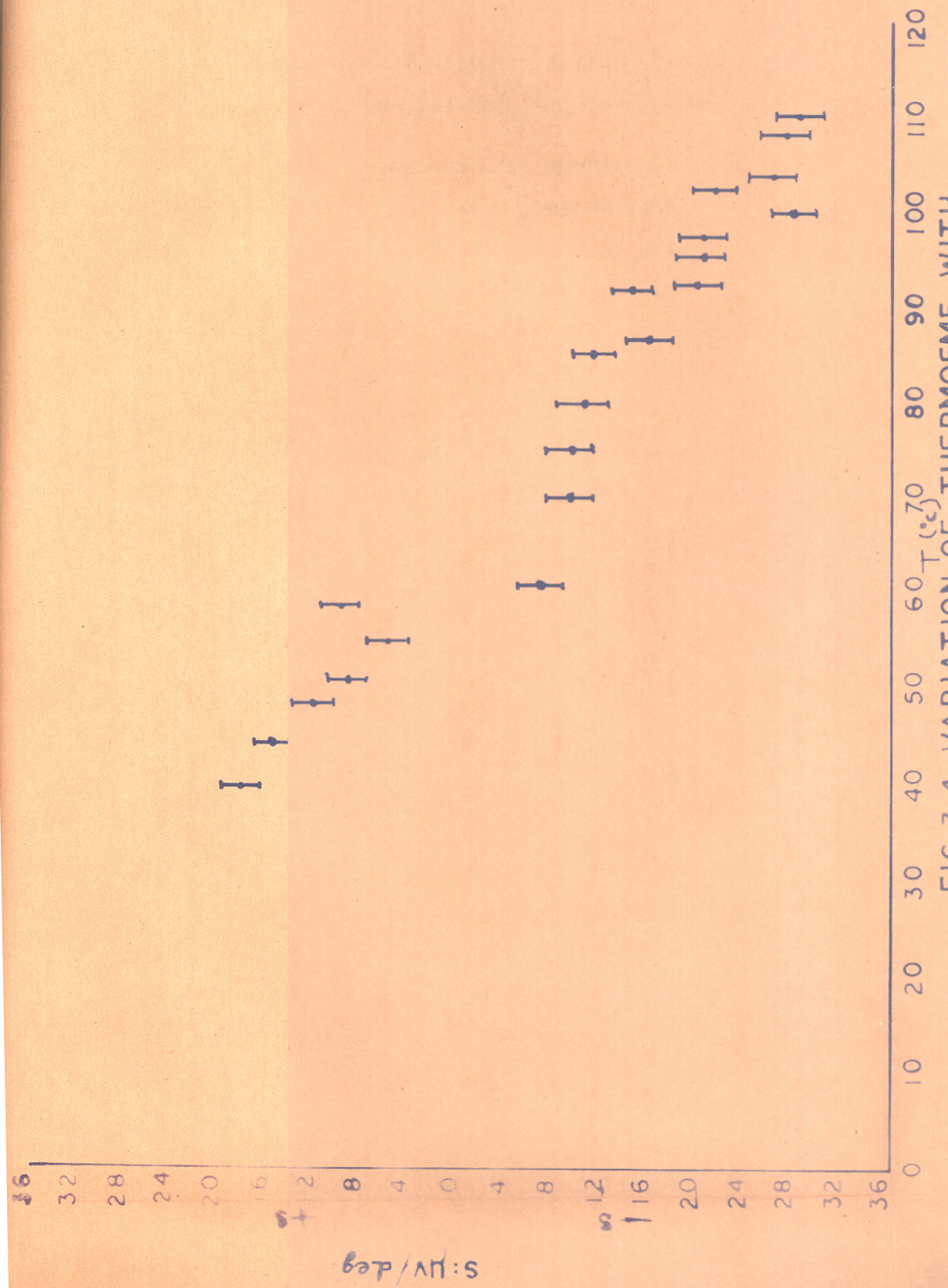


FIG. 3.4 VARIATION OF THERMOEMF WITH TEMPERATURE FOR VP GLASS

The results are consistent with near intrinsic conductivity of the electron-hole type in this material.

There is no reference in literature where thermo emf measurements have been carried out on samples which are in the form of thick films. Every one has used the sample in the form of a pellet, the faces of which were polished. In our case the polishing is completely eliminated. The inter-electrode distance can easily be fixed by using a suitable stencil for the electrodes. The length of the sample is about three times the width. This ratio helps in measuring the temperature at the two ends accurately. It is reported in literature that the vanadium phosphate glasses, with or without other oxides, as n-type semiconductors^{5,7,50,58}. Also, the thermoelectric power is reported to be independent of temperature²².

I-V CHARACTERISTICS

I-V characteristics are plotted in Figures (3.5, 3.6 and 3-7) for (A) Au-VP glass-Au, (B) Au-VP glass-Al and (C) Al-VP glass-Al sandwich structures.

Current-voltage relation is linear upto 36V for the sample (A). Thereafter, there is a tendency for a non-linear relation. The current starts increasing rapidly for every increment of voltage and the current-voltage relation is far from being ohmic.

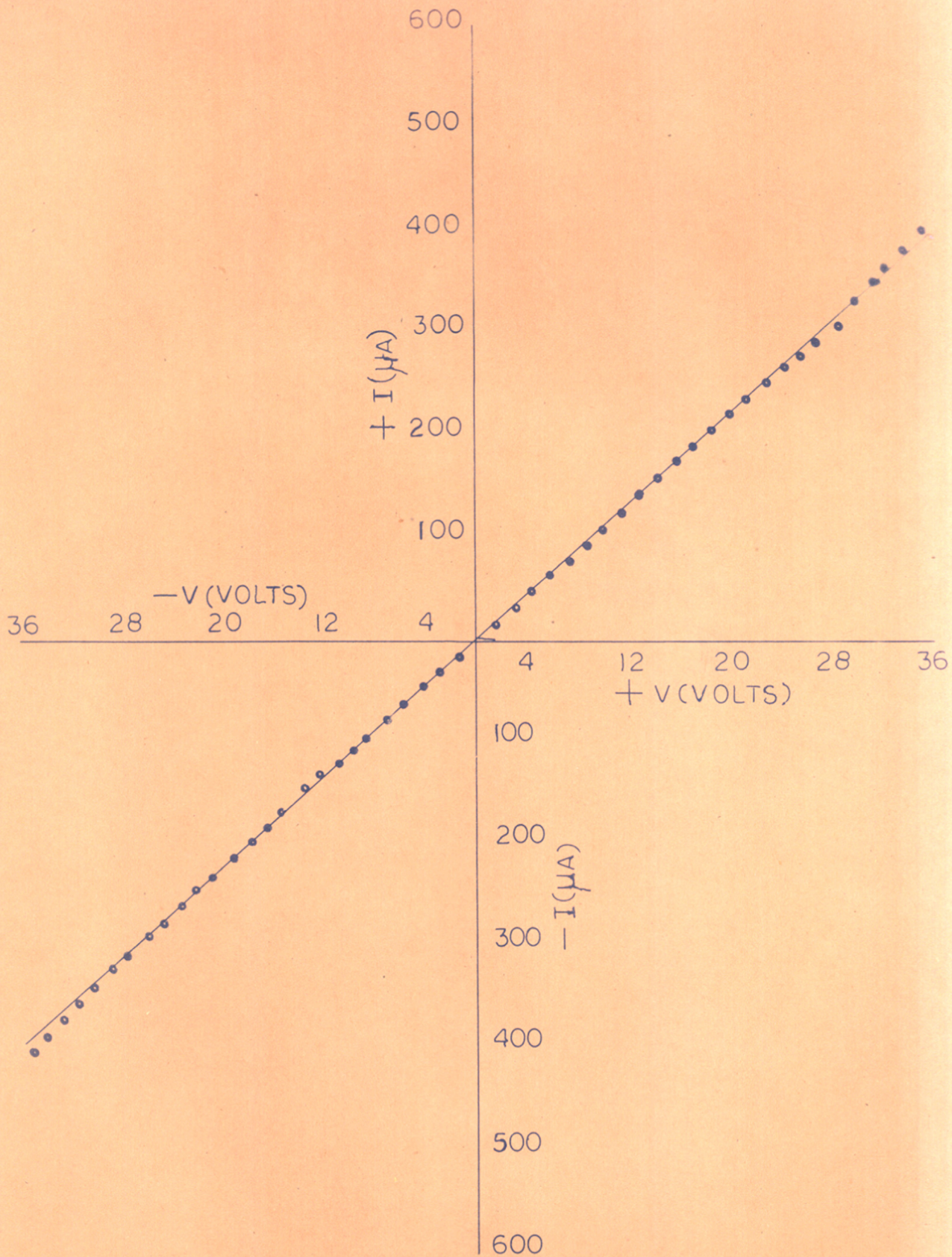


FIG.3.5 I-V CHARACTERISTIC
FOR Au-VP-Au SANDWICH

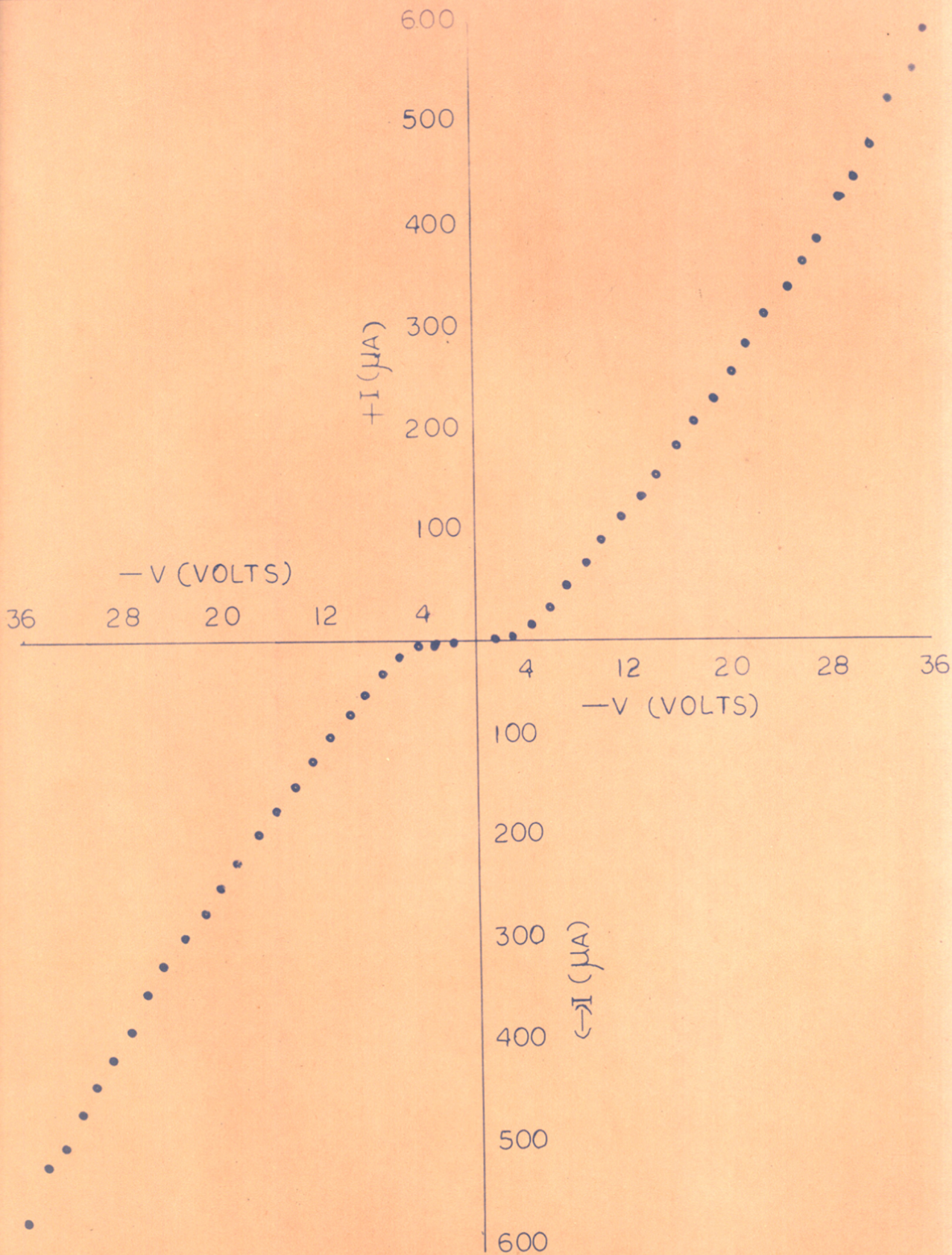


FIG.3.6 I - V CHARACTERISTIC
FOR Au - VP - Al SANDWICH

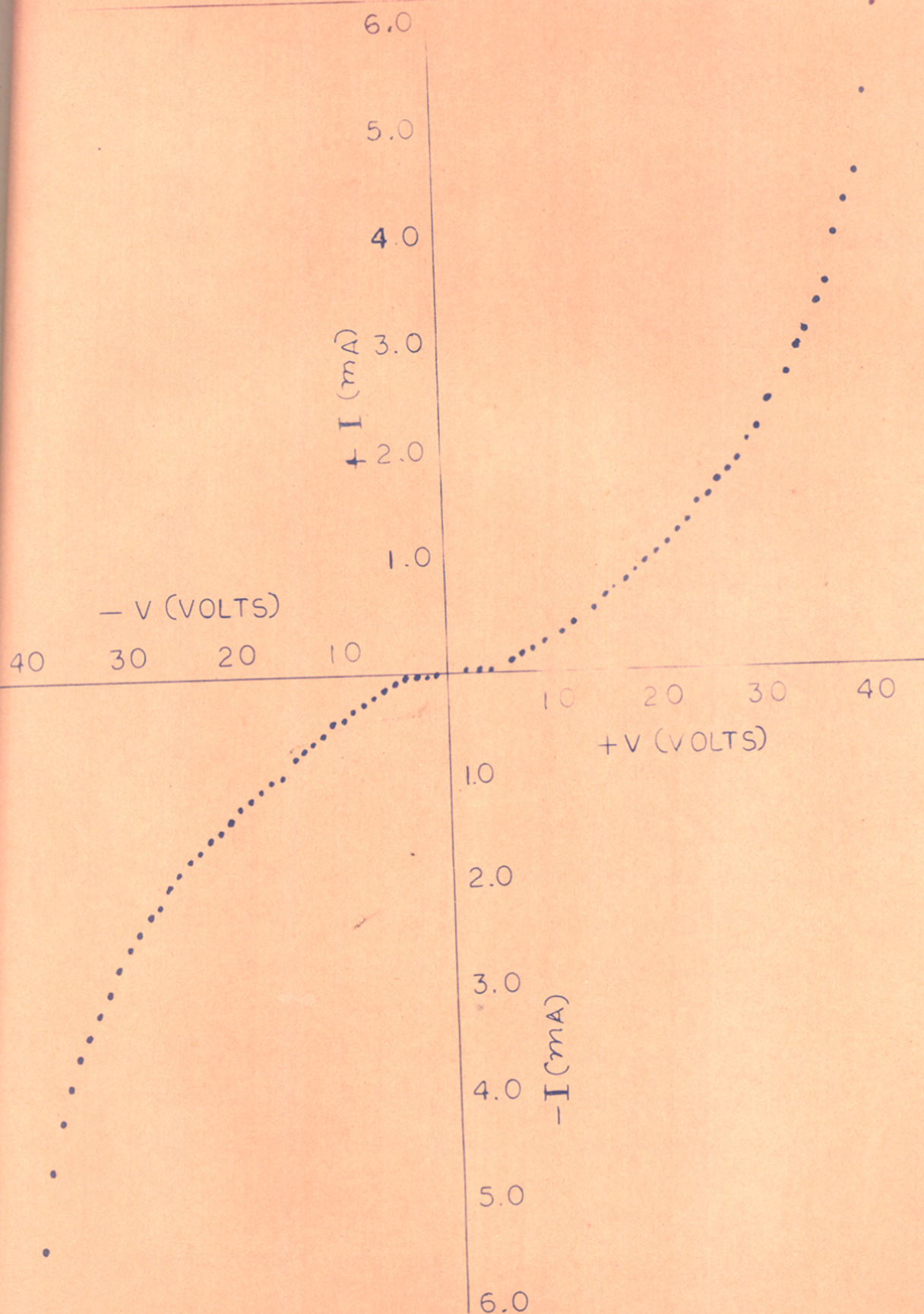


FIG.3.7 I-V CHARACTERISTIC
FOR AL-VP-AL SANDWICH

Whereas in the case of (B), the current-voltage relation is not linear at all (Fig. 3-6). It is asymmetric, non-linear. We can see the beginning of electrode effect on the I-V characteristic from the comparison of the Figures (3-5) and (3-6).

When both the electrodes are of aluminium, the current-voltage relation is symmetric, non-linear. There is a superlinear region where the resistance suddenly drops down at 36V. The current increase is more pronounced in (C) than in (B). In the Figure (3-8), $\sqrt{I}$ is plotted vs applied voltage for (C). The $\sqrt{\text{current-voltage}}$ relation is linear upto 36V. Thereafter the value of $\sqrt{I}$ increases at a faster rate with the increase of the applied voltage.

The holding current at 36V, Fig. (3-7) is 3.4 mA. On further increase of voltage, breakdown takes place and the sample becomes highly resistive. The Fig. (3-9) represents the I-V relation in the postbreakdown condition. Visually, there appears a black spot on the top electrode. The passage of current heats the sample. It is reported that this heat may even boil the low softening vanadium phosphate glass. The resulting effect is that the top electrode gets ruptured.

Switching phenomenon was observed in our samples when aluminium electrodes were used.

Two types of switching (threshold and memory) have been observed in semiconducting glasses⁸¹. In threshold switching, the resistance drops suddenly at a critical field

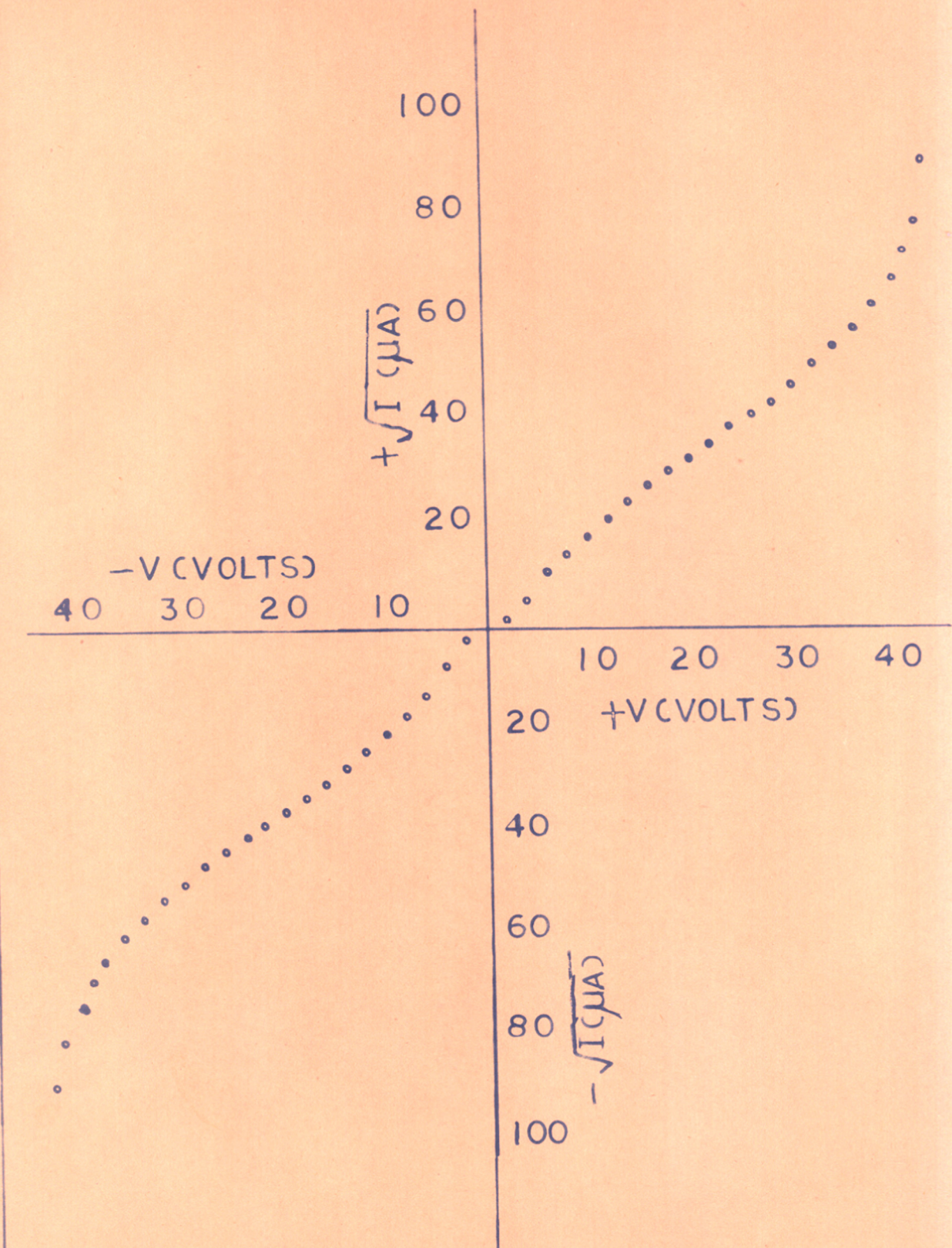


FIG. 3.8 $\sqrt{I}$ -V CHARACTERISTIC
FOR AL-VP-AL SANDWICH

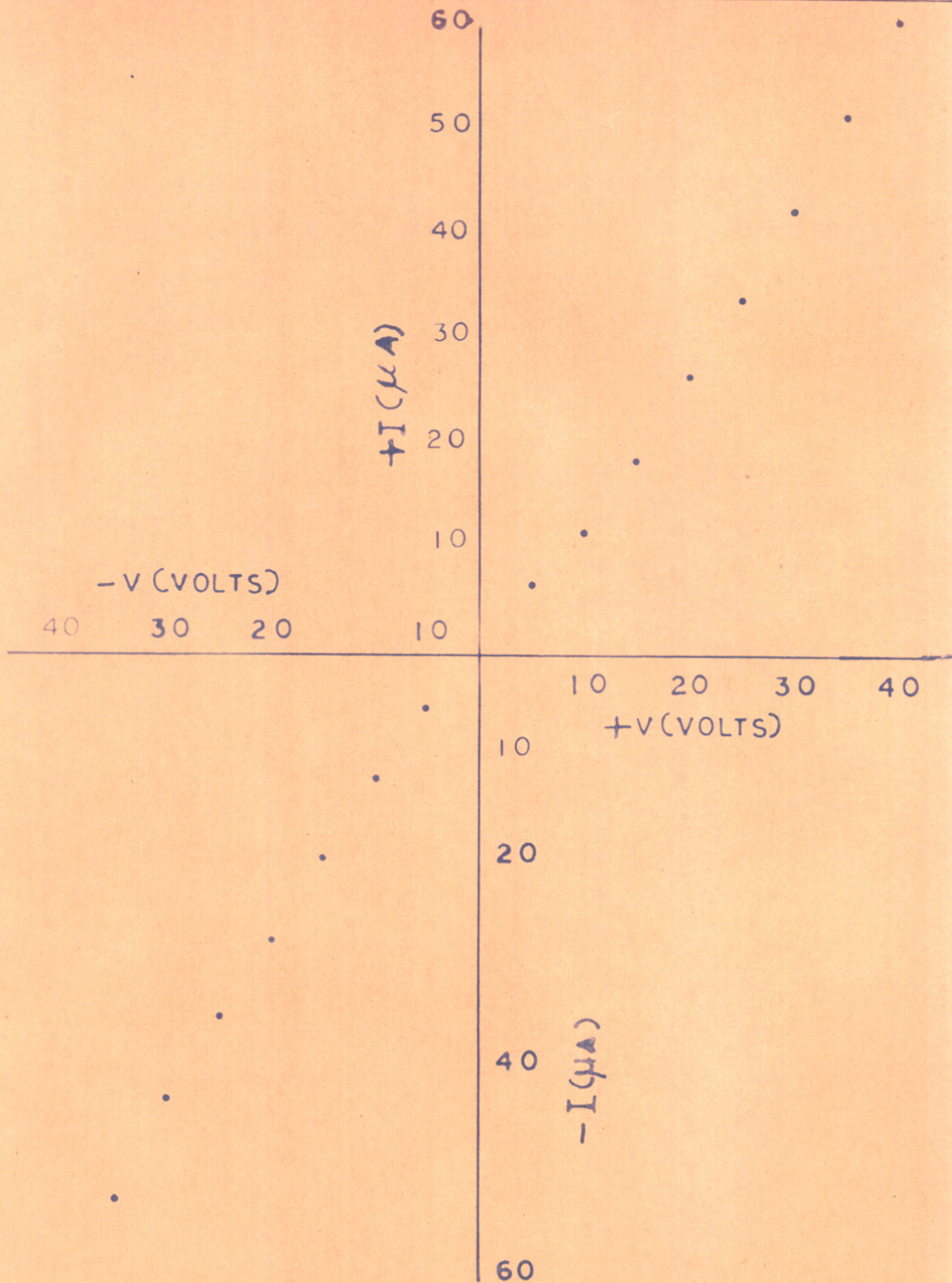


FIG.3.9 I-V CHARACTERISTIC FOR
POST-BREAKDOWN AL-VP-AL SANDWICH

such that the sample becomes a conductor and remains so as long as sufficient current flows. In the case of memory switching, there is a permanent drop in resistance after the application of critical field. The resistance can be restored by the use of a suitable current pulse. The device has thus two states in this case.

Alexander⁷⁸ observed threshold switching in V_2O_5 - P_2O_5 thin layers, obtained by chemical vapour deposition method at 5-10 V with low holding currents. He mentioned that the device could not be switched off after the forming process and remained a short circuit. He used aluminium contacts. He suggested that the switching process as filamentry.

Later Higgins et al.¹⁰⁰ observed threshold switching in sandwich structures of 75 V_2O_5 -25 P_2O_5 made by thick film method. The holding current was 0.25 mA at threshold voltage of 15V. They mentioned that the resistance ratios (R_{off}/R_{on}) were not large compared to those of chalcogenide glass switches. The authors also have suggested that the switching action was thermal and filamentry because the power required to hold the device "on" (~ 15 mw) was less than that required to switch them (~ 50 mw).

Dimitriev et al.¹⁰¹ mentioned that when the inter-electrode distances are sufficiently small, the current-voltage characteristic is no longer governed by the Ohm's law. After a certain threshold voltage has been reached, the resistance drops down abruptly.

We have observed threshold switching in our samples also. The interelectrode distances could be obtained as small as 1 mil. by thick film method. We cannot get such thickness in bulk method. The work of Higgins et al. also support the view that the thickness of the VP glass could be in the range of 30-60 μm to have switching.

Dimitriev et al. further observed that the temperature of the sample influences the threshold voltage. Higher the temperature, lower will be the threshold voltage. Also, V_2O_5 concentration in the sample has similar effect on the threshold voltage.

In order to explain switching they assigned several reasons:

1. Switching is closely related to the process of crystallization of certain highly conducting substances like VO_2 formation which has been proved to have metallic conductivity. It is necessary to melt the highly conductive crystallized channels to bring the device back to 'off' state.
2. A combined action of electronic conduction mechanism and heat breakdown.
3. Interaction between the electrode material and the semiconducting glass which may result in a new compound formation at the interface. This may disturb the carrier mobility and concentration values.

Kaligina et al.^{77,83,98} also have postulated for the switching phenomenon to occur in V_2O_5 - P_2O_5 glasses, the VO_2 formation whose structure is temperature dependent.

The current-voltage characteristics of our samples were also determined under dynamic conditions with oscilloscope (Tetronix 505A). The results are presented in Figures (3.10, 3.11). In the first case, the bottom electrode was gold and for the top electrode, air drying silver paste was used. In the second case, both the electrodes were gold.

Similar effect has been observed in polycrystalline V_2O_5 by Vezzoli and Napier¹⁰². They have reported the effect of pressure and temperature on switching in V_2O_5 . Semiconductor-metallic transition in the sample, as a result of applied voltage, is termed "switched into on-regime". This, they said could be the result of power induced heating or electronic field associated with the voltage or combination of both. The material returns to 'off-regime' when the voltage is removed. The first threshold switch was considered to be the consequence of reaction in the sample. Original orange-yellow colour of the sample was turned to black. This was attributed to power induced heating. Pressure of about 20 K bar increased the threshold power by about 20 times. The greatest pre-switching heating occurred during the superlinear region.

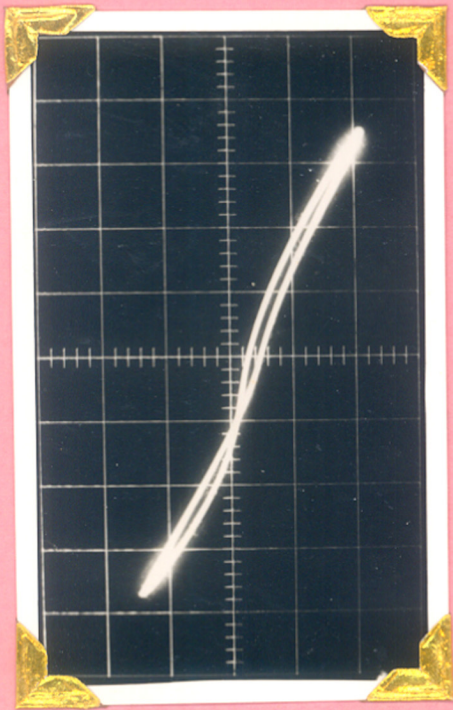


FIG.3.I0. I-V CHARACTERISTIC FOR Au-VP-Ag

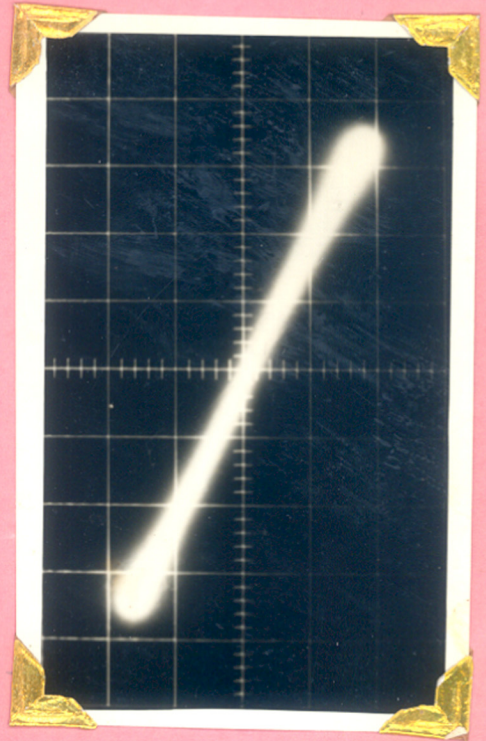


FIG.3.II. I-V CHARACTERISTIC FOR Au-VP-Au

CONCLUSIONS

The activation energy of conduction calculated from the conductivity measurements for our sample is comparable to the reported value in literature. This has proved the suitability of thick film method for preparing the samples.

The I-V characteristics for the Al-VP-Al sandwich structure using thick film method can find good support in Higgins' et al. work. They have reported the threshold switching at 15V threshold voltage. The width of bottom and top electrodes was 0.3 mm and 0.4 mm respectively. In our case, the threshold voltage was 36V and the width of the electrodes was 2 mm. This means that the threshold voltage increases with the electrode width and thus with electrode area. The voltage in our case is about 2.4 times compared to Higgins' value. The electrode width is about 4 times. This can be explained as follows: When voltage is applied across the sandwich sample, its temperature rises due to Joule heating of the sample. Cooling of the sample takes place because of the heat transfer into parallel plate electrodes in a direction perpendicular to the glass electrode interface. If the electrode area is more, then the rate of cooling will be faster. This means that the heat energy input has to compensate the loss due to cooling in addition to heating the sample to have switching taking place.

Since $H = 1/2 VIt$ Joules

where H = heat energy,
 V = applied voltage,
 I = current,
 t = time,

heat energy is directly proportional to the applied voltage. Hence, we have to increase voltage in order to have switching in the sample. This is exactly what has happened in our case. Since the electrode area was more, the threshold voltage has to be large which is our experimental observation also.

The electrode effect on the I-V characteristics of VP glass has been studied which can be seen from Figures 3.2 - 3.4 and 3.7, 3.8.

Thermo emf measurements were made for the first time on thick films of VP glass. The results show that both electrons and holes take part in conduction mechanism. Electron conduction is prominent at high temperatures, whereas hole conduction is prominent at lower temperatures. There is a transition occurring at about 60°C . The results are consistent with near intrinsic conductivity of the electron-hole type in this material.

The thermogravimetric analysis of the samples indicates the formation and crystallization of VO_2 and the

melting temperature of the glass. These results support the results of I-V characteristics, that the formation of VO_2 is responsible for the threshold switching to take place.

In most of the references where switching in semiconducting glasses due to formation of VO_2 is reported, the results are not substantiated by thermal analysis. We have presented DTA/DTG/TG results in support of the observations for the first time.

Conductivity measurements support the thermal nature of switching as the resistance drops at higher temperature.

The studies have established the efficacy of the thick film method of preparing the samples. The method is simple and the technique has scope for further studies if an automatic screen printer is used. Here the effect of several parameters on electrical properties could be studied. Thus the thick film method lends itself as a good processing technique for the characterisation of semiconducting materials.

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