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ELASTIC CONSTANTS AND ELECTRICAL PROPERTIES OF THE SEMICONDUCTING MnO_2-P_2O_5 GLASSES

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ABSTRACT

The elastic moduli and DC-electrical conductivity are studied as a function of composition for the entire vitreous range of the system MnO_2-P_2O_5 that can be prepared by melting MnO_2 and P_2O_5 oxides in open crucibles. The ultrasonic wave velocities (longitudinal and shear), the elastic moduli, Poisson's ratio and the DC-electrical conductivity are found to be sensitive to the glass composition. It is found from these data that the present semiconducting glass system can be divided into three compositional regions. The results are interpreted in terms of changes in the interatomic force constant and the cross-link densities of network bonds.

INTRODUCTION

The dependence of elastic moduli on glass compositions of a number of phosphate glasses has been studied[1-8]. The results showed dis-continuities in elastic constants with composition. This behaviour is qualitatively interpreted in terms of metal ion coordination numbers, stretching force constants and cross link densities of network bonds.

It has been reported[9-15] that the electrical conduction in these glasses takes place as a result of electrons jumping from metal ions with a low valency state to others with a higher valency. However this conduction process is difficult to interpret quantitatively since it is affected by many factors, such as the type and concentration of the metal ions, its proportions in the two valency states, the preparation conditions and the existence of microstructures within the glass matrix.

The present work forms part of a programme to explore what information can be obtained about atomic and molecular configurations in glass, from studies of the compositional dependence of the elastic constants of MnO_2-P_2O_5 glass system. Furthermore the compositional dependence of DC-electrical conductivity for the same glass series is also highlighted.

EXPERIMENTAL TECHNIQUE

Glass Preparation

Manganese-phosphate glasses were prepared from laboratory reagent grades of Analar manganese oxide (MnO_2) and Analar phosphorus pentoxide (P_2O_5), using alumina crucibles heated in an electric furnace, open to the atmosphere. The weighed quantities of these chemicals in appropriate proportions were thoroughly mixed and placed in an electric furnace, held at 350°C for one hour. This allows the P_2O_5 to decompose and react with MnO_2 before melting would ordinary occur. After this heat treatment the mixture was transferred to the second furnace which was already held at a temperature range from 850°C to 980°C for 40 minutes (the highest temperature being applicable to the mixes richest in MnO_2). The glass melts were stirred occasionally with an alumina rod to ensure homogeneous melts. Each melt was cast into two mild-steel molds to form glass rods 2 cm long by 1.5 cm diameter. After casting each glass was immediately transferred to an annealing furnace held at 300°C for one hour. After this time, the furnace was switched off and the glass were allowed to cool to room temperature gradually. This procedure was employed to prepare glasses with a glass formation range from 5 to 60 mole % MnO_2 (starting compositions).

Specimens used for ultrasonic and electrical conductivity measurements were in the form of cylindrical rods of 1.5 cm diameter and 0.5 cm thickness with parallel faces.

The densities of the glasses were measured by the Archimedes method using toluene as the immersion liquid and for comparison of the different glasses only they are accurate to ± 0.001 g cm^{-3}.

Ultrasonic Measurements

The ultrasonic compressional and shear wave velocities were made by the pulse echo technique, using commercial transducers at a frequency of 4 MHz, actuated by an ultrasonic flaw detector (ultrasonoscope ML 32). Details of the techniques are presented elsewhere[5].

The elastic constants of the studied glasses were calculated at room temperature using the measured densities, ρ, and the velocities of longitudinal, V_l, and shear, V_S, waves using the following expressions:

longitudinal modulus	$L = \rho V_l^2$
shear modulus	$G = \rho V_s^2$
bulk modulus	$K = L - (4/3) G$
Poisson's ratio	$\sigma = (V_l^2 - 2V_s^2) / 2(V_\ell^2 - V_s^2)$
Young's modulus	$E = (1 - \sigma) 2 G$

The total maximum error in the measurements of elastic moduli due to changes in specimen thickness (0.02%), velocity (0.05%) and density (0.001%) is therefore about 0.08%.

DC-Electrical Conductivity Measurements

For the measurements of DC-electrical conductivity at room temperature, electrodes were formed by brush painting silver paste. In the present measurements, the current was measured by means of a Keithley electrometer model 616, with a smoothing adjustable power supply (0-1 KV). The fixed voltage of 300 volts was applied.

The DC-electrical conductivity, of each glass sample was calculated by using the expression:

$$\sigma = L / RA$$

where L is the thickness of the sample, A is the area of the electrode and R is the resistance.

RESULTS AND DISCUSSION

The data of table (1) has shown that there are a change in behaviour of the compositional dependence of all the properties examined in this work around 15 and 35 mole % MnO_2 content.

The plots of density and molar volume versus MnO_2 content are given in Fig. 1. The effect of manganese on the glass in region (0 — 15 mole % MnO_2 oxides) was to rupture P=O bonds to form P-O-Mn cross-links. This leads to a compaction of the structure which cause a decrease in the glass molar volume (Fig. 1(b)) and an increase in the glass density (Fig. 1(a)).

Further increase in MnO_2 content the density decreases and molar values increases up to 35 mole % MnO_2 content (Fig. 1). This may be due to the increase of P-O-Mn concentration of larger volume.

As the MnO_2 oxide increases beyond 35 mole %, the density increases while molar volume decreases. This may be due to the increase of saturated O-Mn-bond concentrations.

The addition of MnO_2 to the vitreous P_2O_5 increases both the longitudinal and the shear wave velocities up to 15 mole % MnO_2 oxide (Fig. 2). Beyond 15 mole %, there is a decrease in the ultrasonic wave velocities with further addition of manganese oxide until 35 mole % MnO_2 oxide content. For MnO_2 > 35 mole % the velocities increase again. All the decrease elastic moduli, viz longitudinal, shear, bulk and Young's modulus show the same trend with composition as the acoustic wave velocities (see Fig. 3 (a) and (b)). This may confirm the given explanation of the bond concentration for density and molar volume.

The bond model construction representing the three compositional regions, according to this view, is given in Fig. (4).

Accordingly these results may be interpreted with the light of the model[6], i.e.

$$K = \text{constant.}\ F/(\ell)^n$$

where K is the Bulk modulus, F is the bond stretching force constant, ℓ is the diameter of the atomic rings and n is typically high = 4. This mean that the elastic moduli tend to increase with both cross-link density and the bond stretching force constants. So, the increased amount of cross-linking with increasing content of MnO_2 up to 15 mole % causes the average atomic ring size and Poisson's ratio (see Fig. 5(a)) to decrease and this leads to increase the elastic moduli of the glasses (see Fig. 3).

In the region 15-35 mole % MnO_2 two opposing processes are taking place simultaneously: An increase in cross-link density for the vitreous P_2O_5 from 1 to 2 and also increase the number of weaker Mn-O bonds compared with P-O bonds[16]. At the greater fraction of $Mn\text{-}O_4$ content, the effect of cross-linking is overridden by that of weaker Mn-O bonds and for this reason the elastic moduli decreased with increasing MnO_2 content in this region.

As the MnO_2 oxide increases beyond 35 mole % an increase in the elastic moduli is observed. The increase in elastic moduli may be attributed to the gradual transition of tetrahedral $Mn\text{-}O_4$ (cross-link density = 2) to octahedral $Mn\text{-}O_6$ (cross-link density = 4) (see Fig. 4(c)). However, Poisson's ratio data showed an increase with increasing MnO_2 content beyond 35 mole % in spite of the cross-link density increament. This behaviour might indicate that the manganese ion in octahedral coordination is usually weak directionally; which produced a low ratio of F_b/F (where F_b and F are the bending and stretching force constants, respectively) followed by increasing in Poisson's ratio values (see Fig. 5(a)).

The composition dependence of Debey temperature confirm the detected three compositional regions (Fig. 5(b)).

Figure 6 shows that the DC-electrical conductivity is a composition dependent, where it decreases with the increase in the MnO_2 content up to 15 mole %. This decrease in DC-conductivity may be attributed to the increase in the average cross-link density of glasses which leads to the scattering of the charge carriers. However, in the glass compositional region 15 — 35 mole % an increase in the DC-conductivity is observed (see Fig. 6). This may be due to the decrease of the scattering probably due the increase of molar values and the structure transfer from Fig. 4a to 4b.

As the MnO_2 increases beyond 35 mole % the variation of DC-conductivity shows decreases with the increasing in the MnO_2 content. This may be due to the increase of the scattering factors on the structure transfered from the form of Fig. 4b to Fig. 4c i.e the O-Mn concentration increases.

Table (1): Composition, density, molar volume, longitudinal and shear ultrasound velocities and elastic moduli of MnO_2-P_2O_5 glasses at room temperature

Glass	MnO_2 mole%	Density ($g\ cm^{-3}$)	Molar volume(cm^3)	Ultrasonic wave velocity ($m\ s^{-1}$)		Elastic Moduli *(Kbar)				Poisson's ratio	Debye Temp.(K)
						Long.	Shear	Bulk	Young's		
Pure P_2O_5	-	2.520	56.3	4055	2190	414	121	253	313	0.294	307
M_1	5	2.947	47.2	4406	2469	572	180	332	458	0.271	412
M_2	10	3.165	43.1	5422	2805	930	249	598	656	0.317	486
M_3	15	3.271	40.9	5562	2992	1012	293	621	759	0.296	526
M_4	20	3.012	43.5	5031	2734	762	225	462	581	0.291	470
M_5	30	2.724	46.1	4344	2406	514	158	303	404	0.279	405
M_6	35	2.688	45.6	4281	2343	493	148	296	381	0.286	396
M_7	40	2.829	42.4	4641	2562	609	186	361	476	0.281	444
M_8	50	3.202	35.7	5797	3133	1076	314	657	812	0.294	576
M_9	55	3.425	32.6	6094	3438	1272	405	732	1026	0.267	649
M_{10}	60	3.547	30.7	6609	3578	1549	454	944	1174	0.293	691

* 1 Kbar = $10^8\ N/m^2$

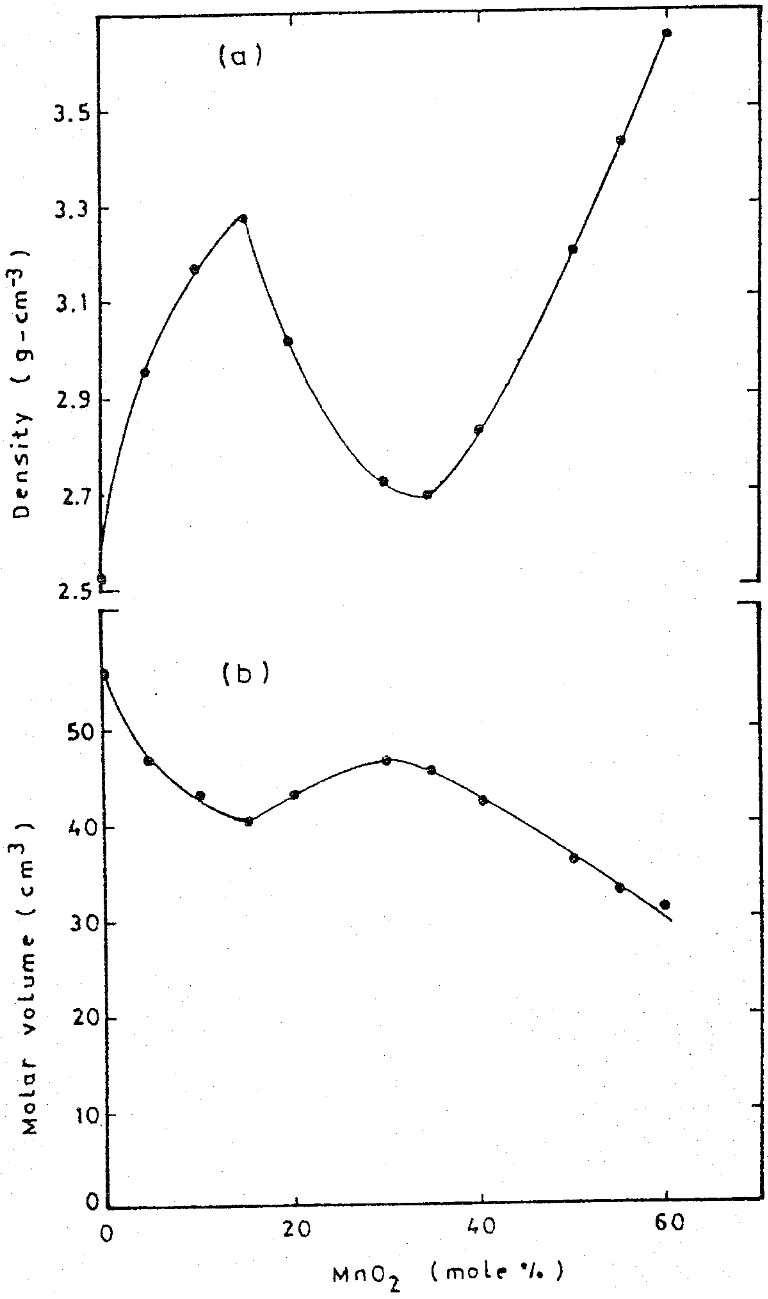

Fig.(1)

Fig. (1): Variations of (a) density and (b) molar volume with MnO_2 mole %.

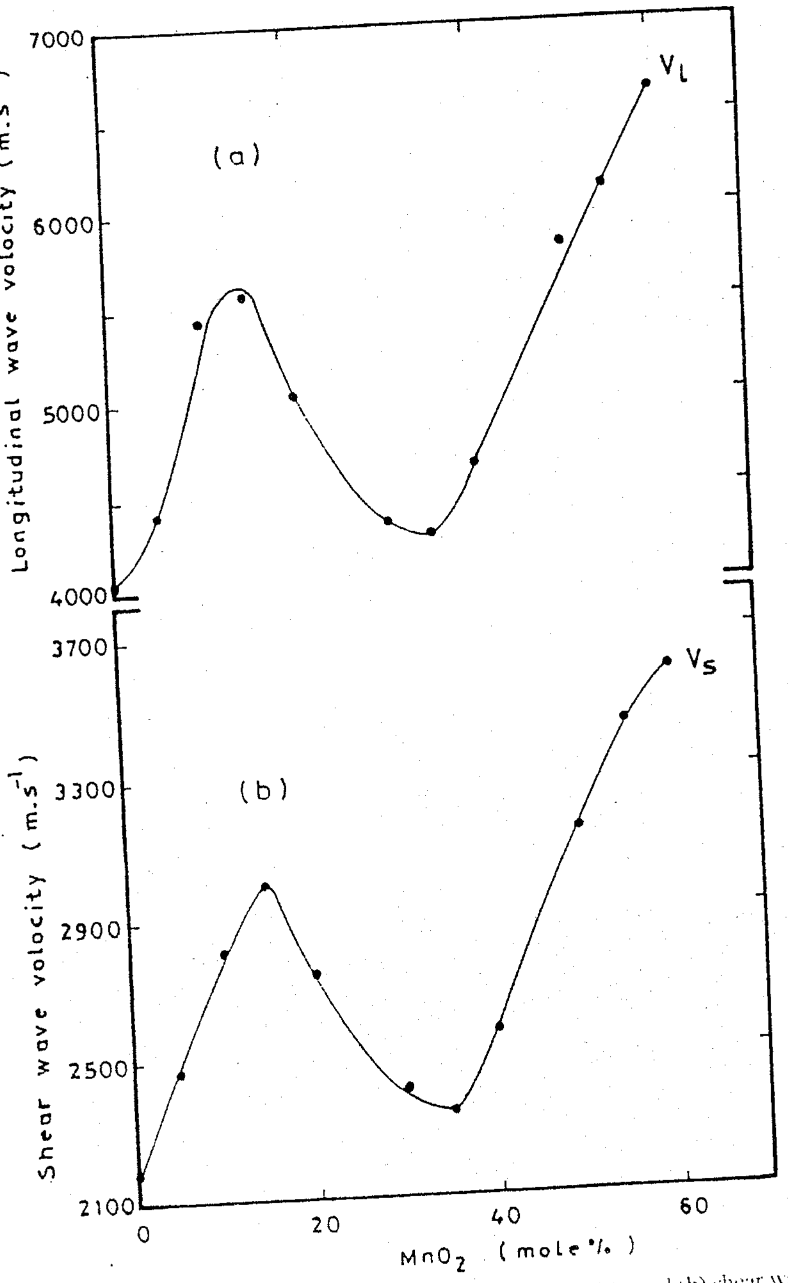

Fig. (2): Dependence of (a) longitudinal wave velocity, V_L, and (b) shear wave velocity, V_S, on the composition of MnO_2-P_2O_5 glasses.

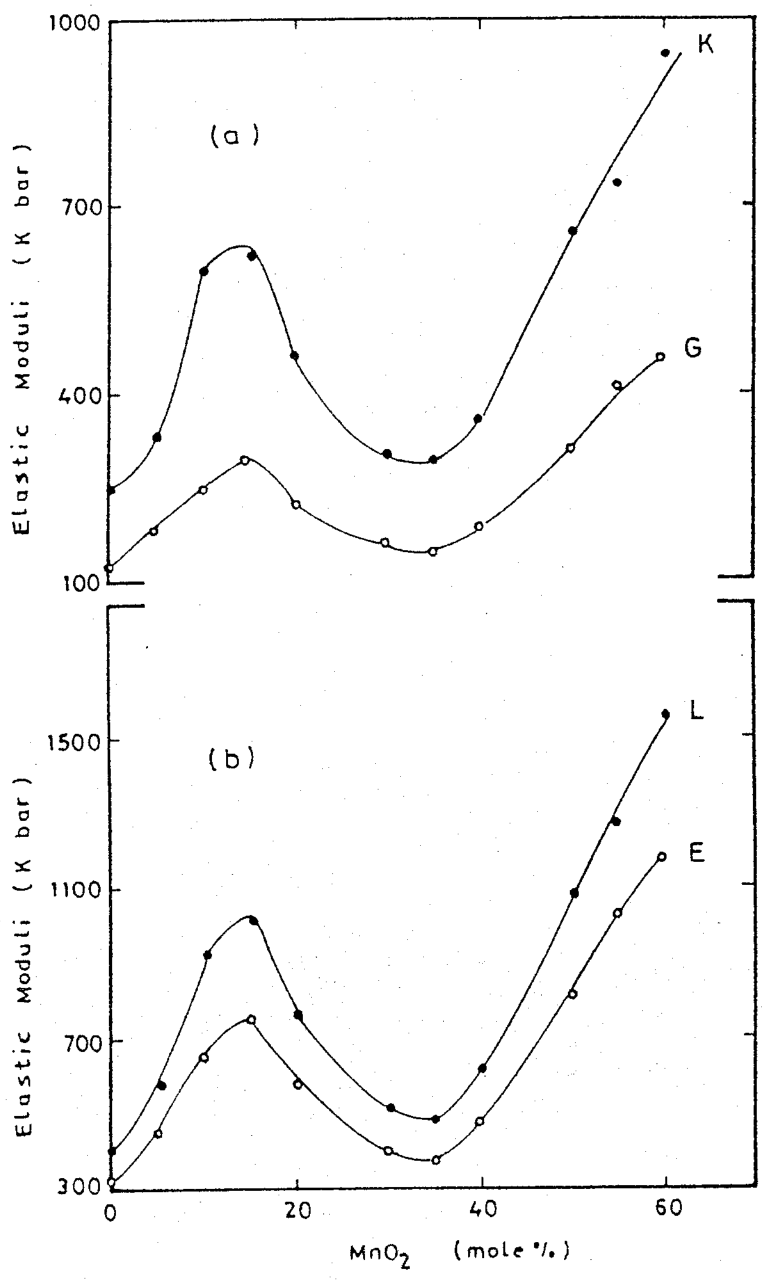

Fig. (3): Compositional dependence of (a) Bulk modulus, K, and shear modulus, G, and (b) longitudinal modulus, L, and Young's modulus, E, in MnO_2-P_2O_5 glasses.

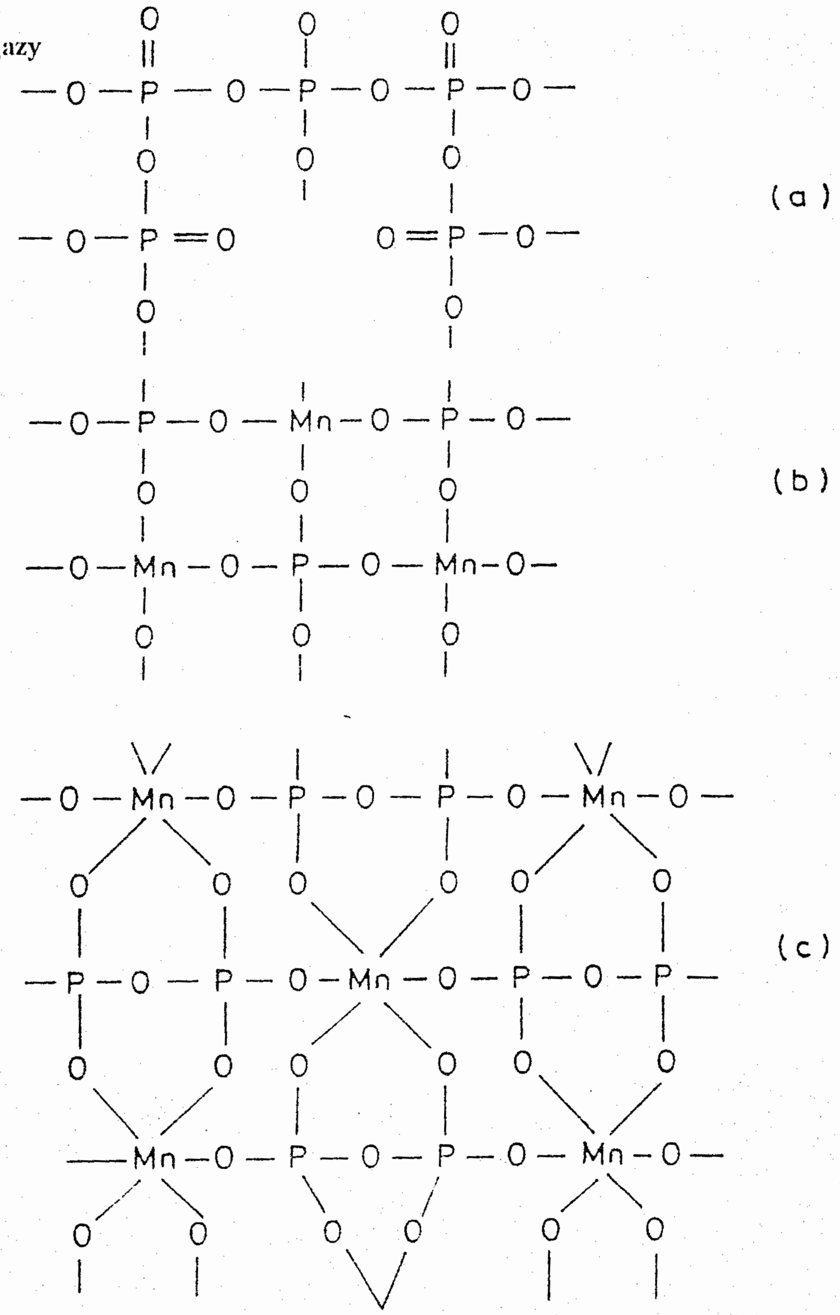

Fig. (4): Schematic two-dimensional representation of the effect of the network modifying MnO_2 oxide on the P_2O_5 network: (a) the P_2O_5 network structure, (b) the structure at 35 mole % MnO_2 oxide and (c) the structure of manganese phosphate glasses when MnO_2 mole % > 35.

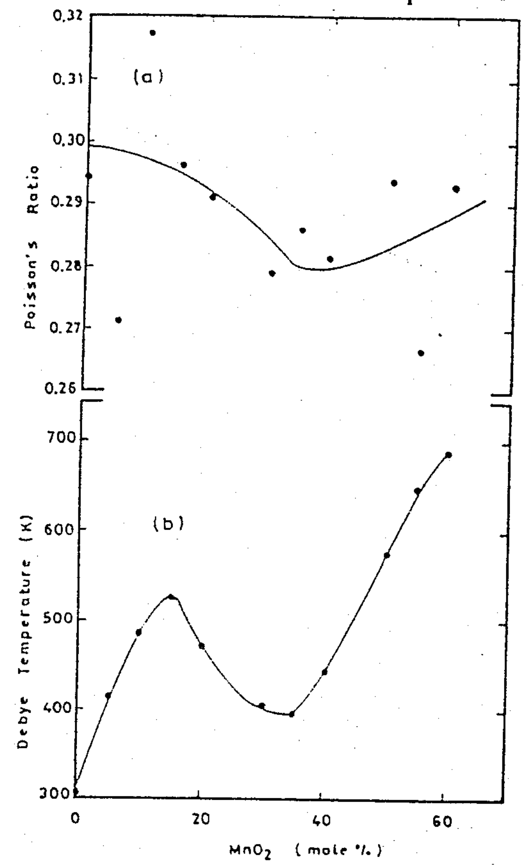

Fig. (5): Variation of (a) Poisson's ratio and (b) Debye temperature with MnO_2 mole %.

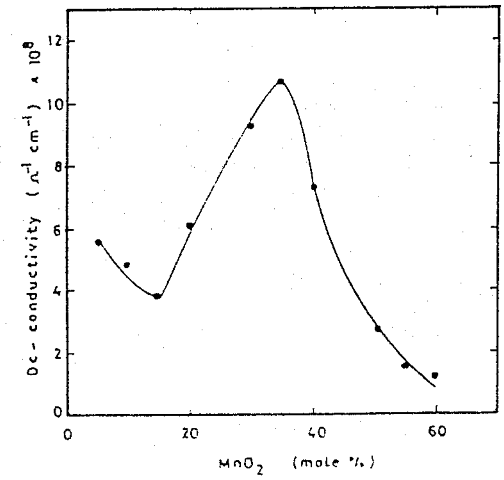

Fig. (6): Compositional dependence of DC-electrical conductivity.

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ثوابت المرونة والخواص الكهربية لزجاج فوسفات المنجنيز شبه الموصل

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الملخص العربى

فى هذه الدراسة قد تم قياس سرعة الموجات الفوق صوتية الطولية والمستعرضة لعينات من زجاج فوسفات المنجنيز بتركيزات مختلفة (١٠٪ إلى ٦٠٪ مول) وأنه باستخدام قيم هذه السرعات والكثافة لهذه العينات أمكن حساب معاملات المرونة الأربعة (الطولى – الحجمى – القصى ومعامل ينج) وكذلك تم حساب نسبة بواسون ودرجة حرارة ديباى . وقد أوضحت النتائج أن هذه القياسات تتغير تغيرا ملحوظا مع تغير نسبة المنجنيز فى الزجاج وهذا نتيجة لتغيير فى التركيب البنائى للعينات – وأيضا فى هذه الدراسة تم قياس التوصيل الكهربى لنفس العينات وتبين أيضا أن القياسات الكهربية تعتمد على تركيز المنجنيز فى الزجاج . وقد أمكن تقسيم مدى التركيزات إلى ثلاث مناطق تبعا للإرتباطات المختلفة لأيون المنجنيز .