Indian J. Phys. **69A** (2), 213 – 222 (1995)

IJP A
– an international journal

Elastic constants and electrical properties of the semiconducting MnO_2-P_2O_5 glasses

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Received 6 October 1994, accepted 8 November 1994

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.

Keywords : Acoustic properties, electrical conductivity, semiconducting phosphate glasses

PACS Nos. : 62.20.Dc, 62.65.+k, 72.80.Ng

1. Introduction

The study of the variation of ultrasonic properties with gradual and wide ranging changes in glass composition provides essential information about atomic and molecular configurations in glass. The dependence of elastic moduli on glass compositions of a number of phosphate glasses has been studied by Farley and Saunders [1], Filed [2], Bridge and Moridi [3], Patel and Bridge [4], Higazy and Bridge [5], Bridge and Higazy [6], Higazy *et al* [7] and Ewaida *et al* [8]. The results showed discontinuities 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.

The electrical conduction processes in the amorphous semiconductors have been an interesting subject. Several investigators [9–15] have paid considerable attention to the study of the electrical properties of phosphate glasses. It has been reported 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

2. 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 alumna 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 moulds 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}.

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 $\sigma = \left(V_l^2 - 2V_s^2\right) / 2\left(V_l^2 - V_s^2\right),$

Young's modulus $E = (1 + \sigma)\,2G.$

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%.

4. 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.

5. Results and discussion

Table 1 contains the compositions, the densities, the molar volumes and the elastic constants of MnO_2-P_2O_5 glasses. The data of this table has shown that there is 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 plot of density versus MnO_2 content (see Figure 1(a)) shows an increase with increasing MnO_2 content up to 15 mole %, which is probably attributable to the effect of adding manganese cations into the vitreous structure of P_2O_5. The sole effect of the entry of manganese into the glass in the first composition region (0–15 mole % MnO_2 oxides) was to rupture P=O bonds and produce P–O–Mn cross-links. This leads to a compaction of the structure which causes a decrease in the glass molar volume (see Figure 1(b)) and an increase in the glass density.

Upon further increase in MnO_2 content, the variation of the density is seen to display a decrease up to 35 mole % MnO_2 content (see Figure 1(a)). This decrease in density indicates a structural change in the glass network, which is accompanied by an increase in the molar volume (see Figure 1(b)).

As MnO_2 oxide increases beyond 35 mole %, substantial increase in density occurs, which is probably attributable to a change in the compaction of the glass structure.

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 = $10^8\,N/m^2$.

Introduction of MnO_2 units in this compositional region (35–60 mole %), leads to a compaction of the structure *i.e.* causes a decrease in the molar volume (see Figure 1(b)).

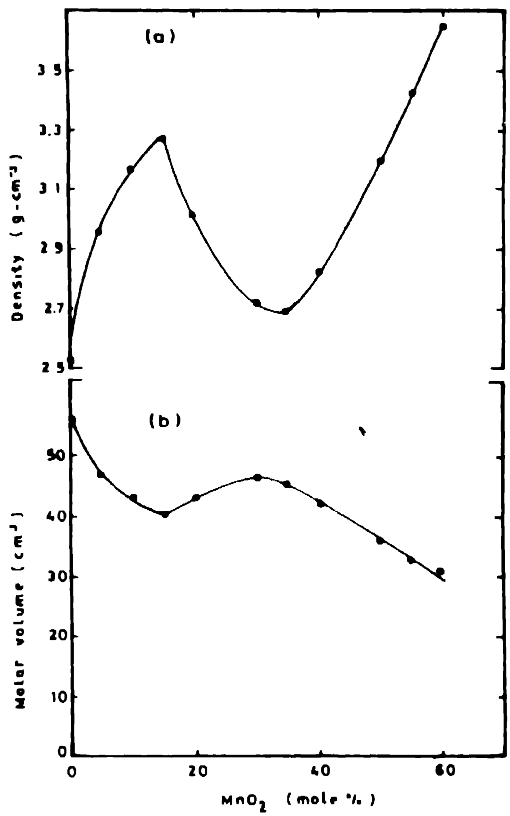

Figure 1. Variations of (a) density and (b) molar volume with MnO_2 mole %

The ultrasonic wave velocities measured in this work are found to be sensitive to the glass composition, as shown in Figures 2(a) and (b). The addition of MnO_2 to the vitreous P_2O_5 structure increases both the longitudinal and the shear wave velocities up to 15 mole % MnO_2 oxide. Beyond 15 mole %, there is a decrease in the ultrasonic wave velocities with further addition of manganese oxide until about 35 mole % MnO_2 oxide content. For high MnO_2 percentages *i.e.* > 35 mole %, the velocities increase again (see Figures 2(a) and (b)). All the elastic moduli, *viz*. longitudinal, shear, bulk and Young's modulus show the same trend as the acoustic wave velocities (see Figures 3(a) and (b)), *i.e.* they exhibit the same '3-composition-regions' behaviour.

It is generally considered that pure vitreous P_2O_5 is built up of an infinite network of PO_4 tetrahedra with each tetrahedron being joined at three corners to other tetrahedra and the remaining unshared oxygen atoms being linked to the phosphorus atoms by a double bonds (see Figure 4(a)). The addition of MnO_4 tetrahedra to P_2O_5 network will transform some of the P=O double bonds into cross-linking (bridging) bonds of the type P–O–Mn and P–O–P (see Figure 4(b)). This increases the average cross-link density of glasses from 1 for the

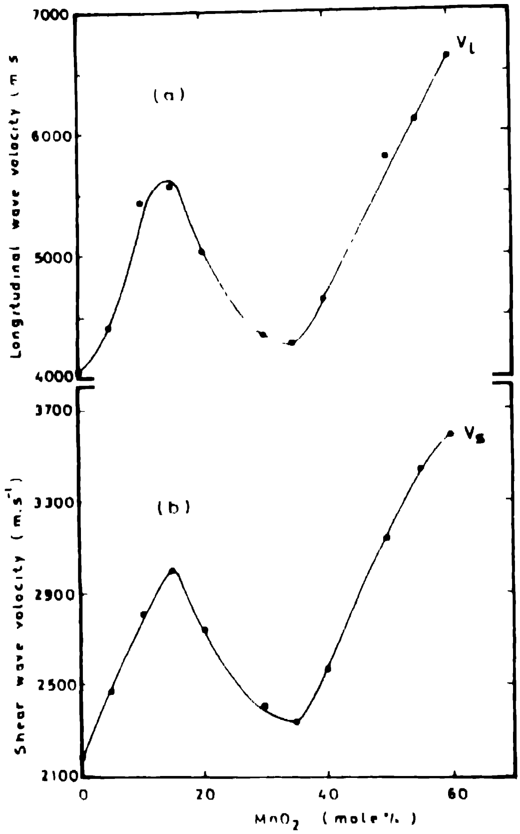

Figure 2. Dependence of (a) longitudinal wave velocity, V_l and (b) shear wave velocity, V_s, on the composition of MnO_2-P_2O_5 glasses

vitreous P_2O_5 to about 2 for the glasses having 35 mole % MnO_2. However, the manganese ions resided in this glass composition range (0–35 mole%) entirely in the tetrahedral form with its lower cross-link density of 2 (see Figure 4(b)). So we may interpret our results according to the models put forward by Bridge and Higazy [6] which is simply expressed in the form

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

where K is the bulk modulus of a structure consisting of a 3-dimensional network of A-O bonds, F is the bond stretching force constant, l is the diameter of the atomic rings *i.e.* the smallest closed circuit of A–O bonds which is dependent on the cross-linking densities of glasses and n is typically high = 4. From the above expression, one can assume 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 Figure 5(a)) to decrease and this leads to increase the elastic moduli of the glasses (see Figure 3).

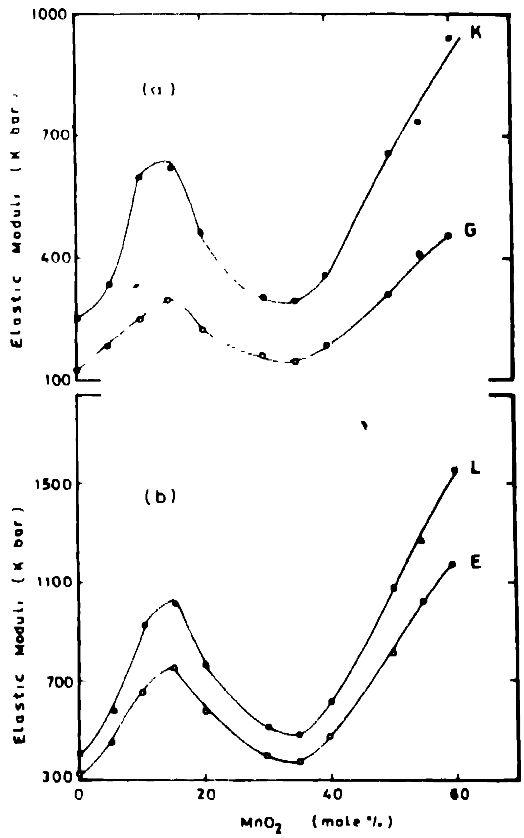

Figure 3. Compositional dependence of (a) bulk modulus, *K*, and shear modulus, *G*, and (b) longitudinal modulus, *L*, and Young's modulus, *E*, in MnO_2-P_2O_5 glasses

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 $Mn–O_4$ content, the effect of cross-linking is overridden by that of weaker Mn–O bonds and for this reason, the elastic moduli decreases with increasing MnO_2 content in this glass compositional range (see Figure 3).

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 $Mn–O_4$ (cross-link density = 2) to octahedral $Mn–O_6$ (cross-link density = 4) (see Figure 4(c)). However, Poisson's ratio data shows an increase with increasing MnO_2 content beyond 35 mole % in spite of the fact that the cross-link density increases. This behaviour might indicate that the manganese ion in octahedral coordination is usually weak directionally;

which produces a low ratio of F_b/F (where F_b and F are the bending and stretching force constants, respectively) followed by an increase in Poisson's ratio values (see Figure 5(a)).

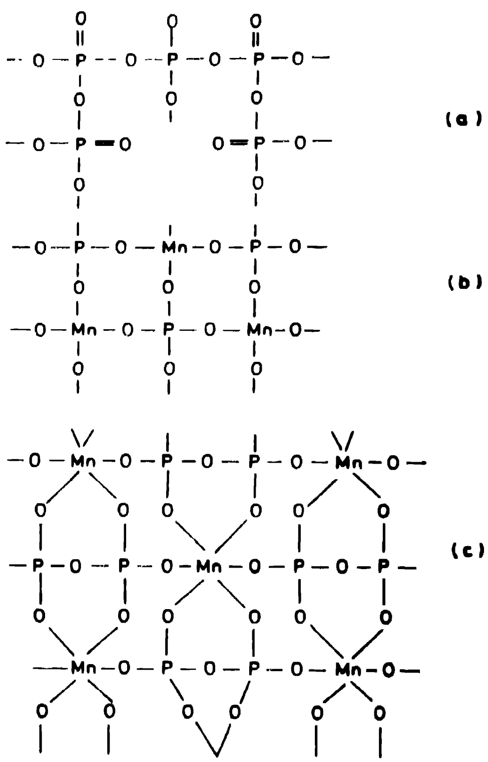

Figure 4. Schematic two-dimensional representation of the effect of the network modifying MnO_2 oxide on the P_2O_5 network (a) the P_2O_5 network structure, (b) the structure at 35 mole % MnO_2 oxide and (c) the structure of manganese phosphate glasses when MnO_2 mole % > 35.

The variation of Debye temperature with MnO_2 content (see Figure 5(b)) showed the same three compositional regions which had been found in the compositional dependence of the elastic moduli.

The general condition for semiconducting behaviour in transition metal oxide glasses, is that the transition metal ion should exist in more than one valency state so that conduction can take place by the transfer of electrons from low to high valency states. In the present investigation, the conduction may take place by the hopping of an electron directly between occupied Mn^{2+} ($3d^5$) and unoccupied Mn^{3+}($3d^4$) sites. also, it is generally considered that the conduction-changes in transition metal oxide glasses are not only due to the concentration of free change carriers but are also due to their mobility.

Figure 6 shows that the DC-electrical conductivity is 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

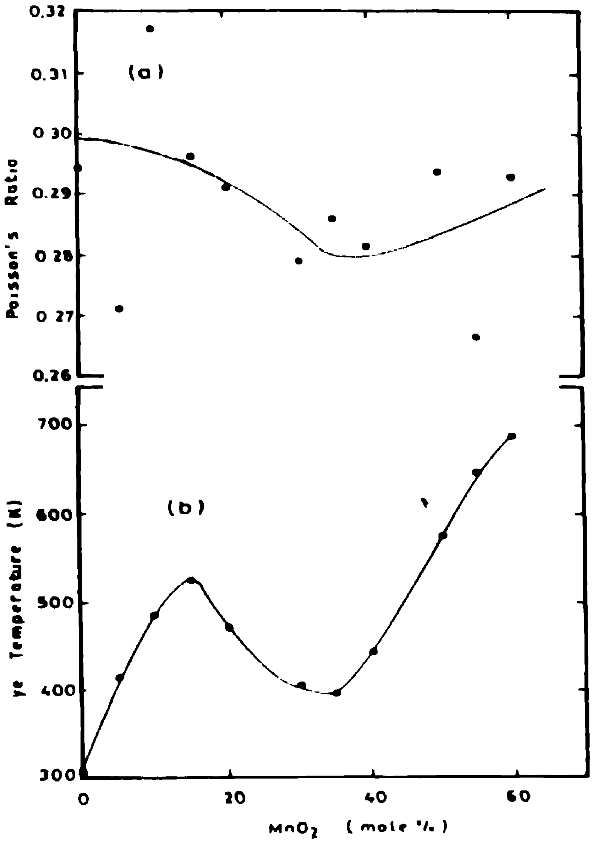

Figure 5. Variation of (a) Poisson's ratio and (b) Debye temperature with MnO_2 mole %

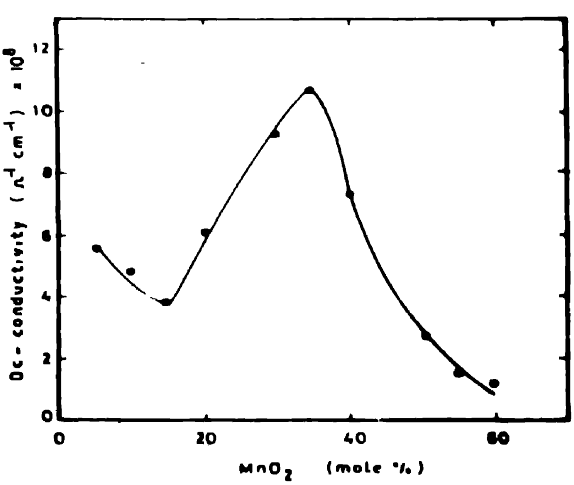

Figure 6. Compositional dependence of DC-electrical conductivity

which causes the mobility to decrease. However, in the glass compositional region 15–35 mole %, an increase in the DC-conductivity is observed (see Figure 6). As MnO_2 is increased in this compositional region, the effect of cross-linking is overridden by that of the free charge carriers concentrations (free electron density for Mn = 16.5 × 10^{22} cm^{-3}).

As MnO_2 increases beyond 35 mole %, DC-conductivity decrease with the increase in the MnO_2 content. In the glass compositional region (35–60 mole %), we believe that the manganese ions are gradually coordinated with six oxygen anions. Therefore, we ascribe the decrease in DC-conductivity with MnO_2 oxide content to a gradual transition from Mn–O_4 tetrahedra (cross-link density = 2) to Mn–O_6 octahedral (cross-link density = 4) *i.e.* due to the decrease in the free carriers charge mobility.

6. Conclusion

From the foregoing analysis, it is found that all the properties studied in the present investigations are found to be sensitive to the glass composition. On this basis, it is found that the present glass system can be divided into three distinct compositional regions.

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