Sci. J. Fac. Sci. Monoufia Univ., Vol. III, (Phys. & Maths.) 1989.

THERMOELECTRIC POWER OF THE VITREOUS SYSTEM Bi_2O_3 - P_2O_5

BY
A.A Higazy, M.M. EL-Zaidia.
Phys. Dept., Faculty of Science EL-Monoufia University, Shebin El-Koom, Egypt.

And
M.A.T.Dawoud and A.M.Abo-Arayis
Phys. and Math. Dept., Faculty of Electronic Engineering, El-Monoufia University, Monouf, Egypt.

ABSTRACT

Thermoelectric power measurements for bismuth-phosphate glasses prepared from pure oxides are carried out in the temperature range from 330° K up to 580 ° K. The curves of thermoelectric power (S) versus temperature go through - ve and + ve values of S. This suggests that the charge carriers are electrons and holes. Thermoelectric power and activation energy data are found to be sensitive to the glass composition. Results indicate a structural change in the glass network around 25 Bi_2O_3 mole %.

INTRODUCTION

The thermoelectric power phenomenon in the material under test has been investigated by many workers [1-8]. They have reported that the thermoelectric power (Seebeck coefficient) could be used to elucidate the nature of the transport mechanisms in materials.It is well Known that, for an n-type crystalline semiconductor [6], Seebeck coefficient S, is given by

$$S = \frac{k}{e}\left(\frac{E_c - E_f}{KT} + A\right) \qquad (1)$$

where K is Boltzmann's constant, e is the electronic charge, E_c

and E_F are the energies of the conduction band and the ferm level, respectively and A is a constant (where A.K.T is the average energy of the transported electrons measured with respect to E_c). The value of A depends on the nature of the scattering process. Mott and Davis [9] claimed that A is normally a constant ranging between 2 and 4. If the current is carried by holes the sign of S is reversed and (E_c - E_F) is replaced by (E_F - E_v).

In amorphous semiconductors [9] A is expected to be equal to unity when current is carried in extended states; and E_c or E_v refers to the appropriate mobility edges. For current carried in localized states at the band edges, A will again be small and E_c and E_v are to be replaced by E_A and E_B, respectively (see Fig. 1). The sign of S is therefore a reliable indicator of whether the material is n - type or p - type. A plot of S against 1/T has a slope that yields E(0), as does a plot of $\ln\sigma$ against 1/T, and the intercept on the S axis at 1/T = 0 yields the temperature coefficient of the activation energy for conduction. Alternatively a plot of the Peltier coefficient Π = ST versus T yields γ from its slope.

In this work, thermoelectric power measurements of Bi_2O_3-P_2O_5 glass series as a function of composition and temperature (in the range from 330 °K to 580 °K) are performed.

EXPERIMENTAL PROCEDURE

1-Preparation of glasses :

Bi_2O_3 - P_2O_5 glasses were prepared by melting the

appropriate mixture of Analar phosphorous pentoxide and Analar bismuth oxide in alumina crucibles. The mixture was placed in an electric furnace, held at 400° C for one hour. This allows the P_2O_5 to decompose and react with Bi_2O_3 before it reaches its melting point. After this treatment the mixture was transferred to the second furnace which was already at a temperature between 950° C and 1100° C, for 30 minutes (the highest temperature being applicable to the mixture with highest percentage of Bi_2O_3). The glass melts were shaken occasionally and casted into two mild - steel moulds to form glass rods 1 cm long by 1.6 cm diameter. Details of the preparation technique and chemical analysis of these glasses are presented elsewhere [11].

2- Thermoelectric power measurements

The glass sample was placed between two platinum electrodes. The source of heat consisted of an electric heater provided at the remote end of one bar and keeping the remote end of another bar cold. The whole system was introduced in a temperature regulated oven.Two thin sheets of mica were inserted between the platinum electrodes and the Upper and lower bars , in order to achieve good electrical insulation of the samples. The system used is illustrated elsewhere [12]. The temperature difference between both surfaces of the sample was measured by copper - constantan thermocouples. The voltage generated ΔV due to the temperature difference ΔT between the two surfaces of the sample was measured using Auto Digital Multimeter (Type kiethly 175).

RESULTS AND DISCUSSION

The temperature dependence of the thermoelectric power S for five qlass samples of different compositions, see table 1, are shown in Fiq. (2), in the temperature range from 330° K to 580° K. The results show that in general the absolute values of S decrease with increasing the Bi_2O_3 contents from 7.50 mole % up to 40.25 mole %. This is probably due to carrier scattering with lattice defects created by the presence of Bi_2O_3 which exists as impurity centers particularly at higher temperatures. It may be also due to the flux of phonons proceeding from the hot to cold end which drags a larger number of electrons [15]. Moreover it is known that the thermoelectric power produced from metal - semiconductor thermocouple is larger than the one produced from metal - metal thermocouple i.e. if the sample becomes more metallic, S will decrease. This is in agreement with the results of sample B5, where the metal oxide occupies 40.25% of the glass matrix, giving very small values of S.

Table (1) shows the contents of Bi_2O_3 for each sample along with the carrier mobilities at different temperatures. The carrier concentration n for the various samples at different temperatures are given in table [2], it shows that n is nearly constant for each sample over the whole temperature range.

The results of the first sample B1 which has the smallest metal content (Bi_2O_3 = 7.50 mole %) suggest that donor centers are created giving n-type semiconductor with a large value of S, the -ve values of S indicate that the charge carriers are

electrons. The temperature dependence of S for this sample shows that its absolute value decreases with temperature in most of the temperature range, except for a small region from T = 460° K to T = 520° K, where we observe an anomalous increase of S. The decrease of the absolute value of S may be due to the increase of the mobility .

Sample B2 with higher Bi_2O_3 content than B1 gives lower absolute value of S , with still -ve charge carriers. The temperature dependence of S for sample B2 is very simillar to that of sample B1. For sample B3 with still higher Bi_2O_3 content the absolute value of S is smaller than those for samples B1 and B2. But it is important to point out that S has +ve and -ve values in different temperature ranges, which indicates that the carriers are electrons and holes, but each type dominates in different temperature range.This result suggests a begining of a structural change in the glass network at about 20 Bi_2O_3 mole %. For sample B4 with higher Bi_2O_3 content the absolute value of S is still smaller and approaches zero at higher temperature. This sample also contains electrons and holes as charge carriers.

Finally for sample B5 with the highest content of Bi_2O_3, it shows the smallest value of S . The dramatic decrease of S for this sample may be due to the large value of carrier mobility and the samall value of carrier concentration. The results of thermoelectric power S and the activation energy E obtained in this work are found to be strongly dependant on the Bi_2O_3 contents in the present glass system (see Figs. 3 and 4).

The variations of S with Bi_2O_3 contents show minimum

values around 25 mole % indicating that structural changes occur in the present glass system around 25 Bi_2O_3 mole%.

CONCLUSION

Thermoelectric power and activation energy data are found to be sensitive to the glass composition. The results indicate a structural change in the glass network in the range between 20-25 Bi_2O_3 mole%.

It is clear from the curves of S versus T and S versus Bi_2O_3 contents that S changes sign between -ve and +ve values. This suggests the presence of electrons and holes as charge carriers and each type dominates in certain temperature range, that is to say samples go through P-type to N-type changes at particular temperatures, those temperatures are compositional dependant. These results are in agreement with similar results obtained for the temperature and compositional dependence of the thermal conductivity obtained before [13 and 14].

ACKNOWLEDGEMENT

The Authors would like to express thier deep gratitude to professor A. ABDEL-GHANY and Dr. A. ABDEL-SATTAR, Faculty of Science Ain Shams university, for their contineous assistance throughout this work and for providing research facilities. Also thanks are extended to professor A. ETA for his valiable advice.

Table (1): The mobility μ for the various samples at different temperatures.

Sample	Bi_2O_3 mole%	T=340 K	T=440 K	T=520 K	T=580 K
B_1	7.50	1.8×10^{-12}	1.0×10^{-8}	4×10^{-7}	3×10^{-6}
B_2	16.99	1.0×10^{-16}	1.2×10^{-12}	3×10^{-11}	3×10^{-9}
B_3	19.67	3.0×10^{-18}	8.3×10^{-14}	5.1×10^{-11}	7.2×10^{-10}
B_4	35.33	9.3×10^{-11}	2.1×10^{-7}	7.1×10^{-6}	5×10^{-5}
B_5	40.25	---	1.4×10^{-5}	2.7×10^{-4}	9.3×10^{-4}

Table (2): The carrier concentration n for the various samples at different temperatures.

Sample	T=340 K	T=440 K	T=520 K	T=580 K
B_1	1.0×10^{20}	2.1×10^{20}	1.8×10^{20}	2.1×10^{20}
B_2	1.3×10^{22}	1.0×10^{22}	1.5×10^{22}	3.9×10^{22}
B_3	1.8×10^{2}	5.2×10^{22}	5.1×10^{22}	3.4×10^{22}
B_4	6.7×10^{16}	2.0×10^{16}	5.1×10^{16}	1.2×10^{17}
B_5	---	8.0×10^{14}	1.3×10^{15}	4.1×10^{15}

REFERENCES

1. W.J.Turner, A.S.Fishler and W.F.Rease, Phys.Rev.,121, 759 (1961).

2. H.K.Rocksted, R.Flasck and S.Iwasa, J.Non Crystall. Solids, 8(10), 326 (1972).

3. K. Al Zewel, M.M. Abou Sekkina and Z.M. Hanafi, Egypt. J. Phys.,12 No.1, 51 (1980).

4. T.E. Whall, J.Phys. C: Solid state Phys. 14,L 887(1981).

5. V.A.M. Brabers, H.Meuter and Z. Simsa, Solid State Communication, 45 NO.9, 807 (1983).

6. A.A.Ghani, S.A. Mazen and A.H. Ashour, Phys. Stat. Sol. (a), 84, 337 (1984).

7. M. Kitao, K. Yoshie and S.Yamada, Phys. Stat. Sol. (a),91, 271 (1985).

8. A.L. Eatah, A.A. Ghani and E.El-Faramawy, Phys. Stat. Sol. (a), 105, 231 (1988).

9. N.F. Mott and E.A. Davis, Electronic Processes in Non-Crystalline Materials 2nd Ed, Oxford Univ. Press.(1979).

10. N.F. Mott, AdV. Physics , 16, 49 (1967).

11. A.A.Higazy, M.A.Ewaida, A.Hussein and R.M.El-Bahnasawy, Indian J.Phys. 63A (2), 124 (1989).

12. A.ABDEL SATTAR, Ph.D thesis (1988). Faculty of science, AIN Shams University. CAIRO

13. M.M. EL-Zaidia, A.A. Higazy, M.A.T. Dawoud and A. Abo-Arayis, Submitted to Journal of materials science (1987).

14 M.A.T. Dawoud, A.A. Higazy, M.M. El-Zaidia and A. Abo-Arayis, submetted to Indian Journal of Technology (1988).

15. B. Grigas and M. Mikalkvicius, Fiz. Tverd Tela, 7, 3649, (1965).

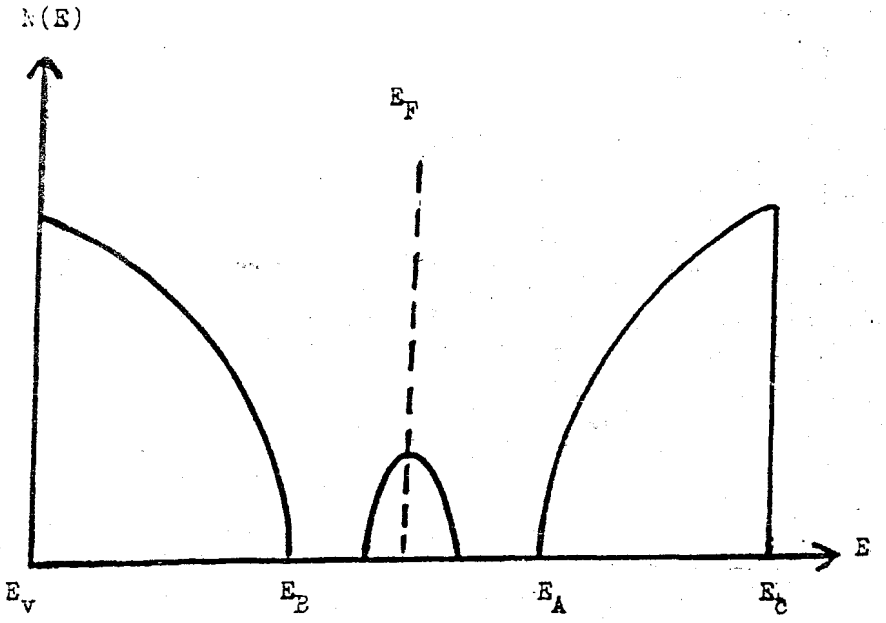

Fig. (1): Proposed band structure model for semiconductors, the density of states N(E) against energy E. (after Mott "10").

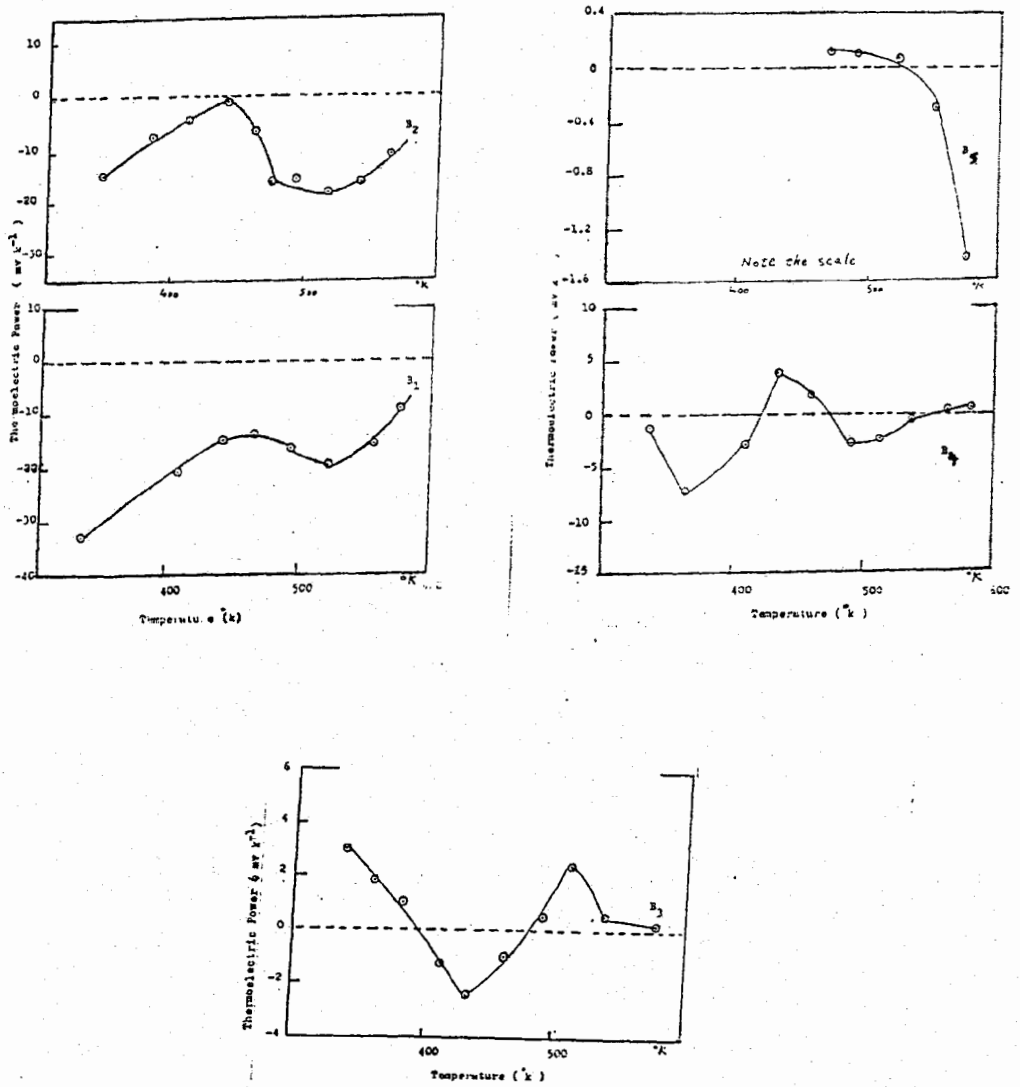

Fig. (2): The temperature dependence of thermoelectric power S for samples B_1 , B_2, B_3 , B_4 and B_5 .

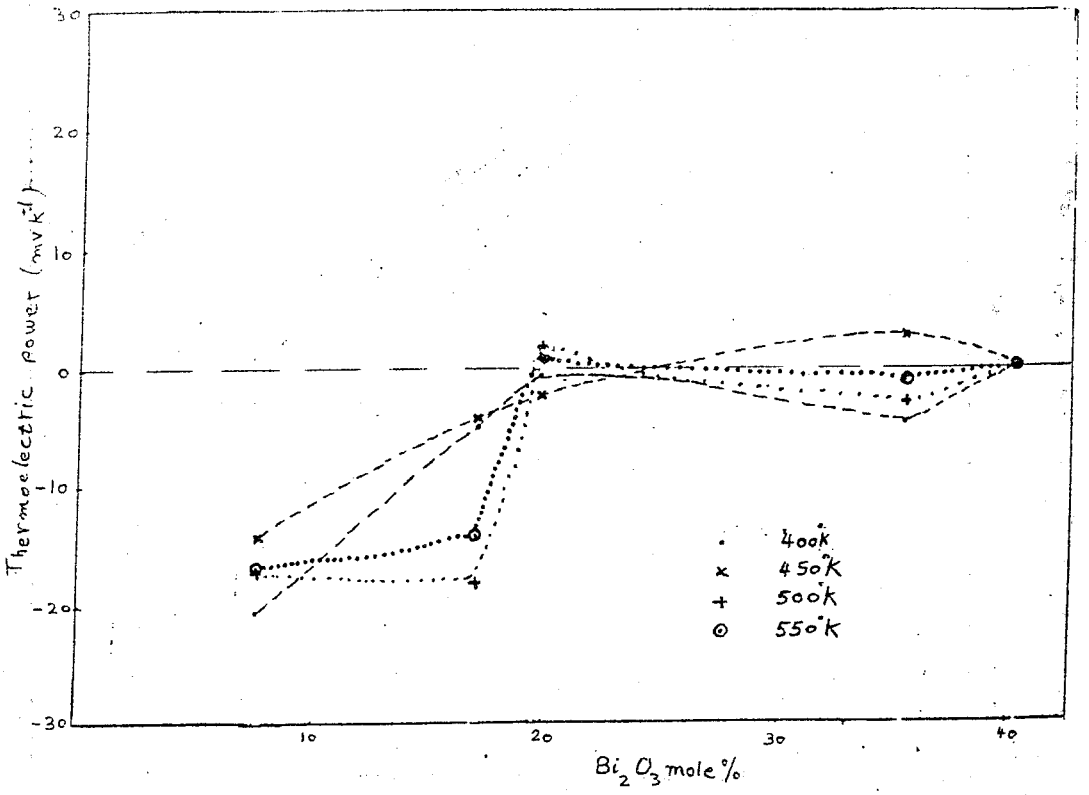

Fig. (3): The dependence of thermoelectric power S on the persentage of the presence of Bi_2O_3. in the samples (compositional dependence), at different temperatures.

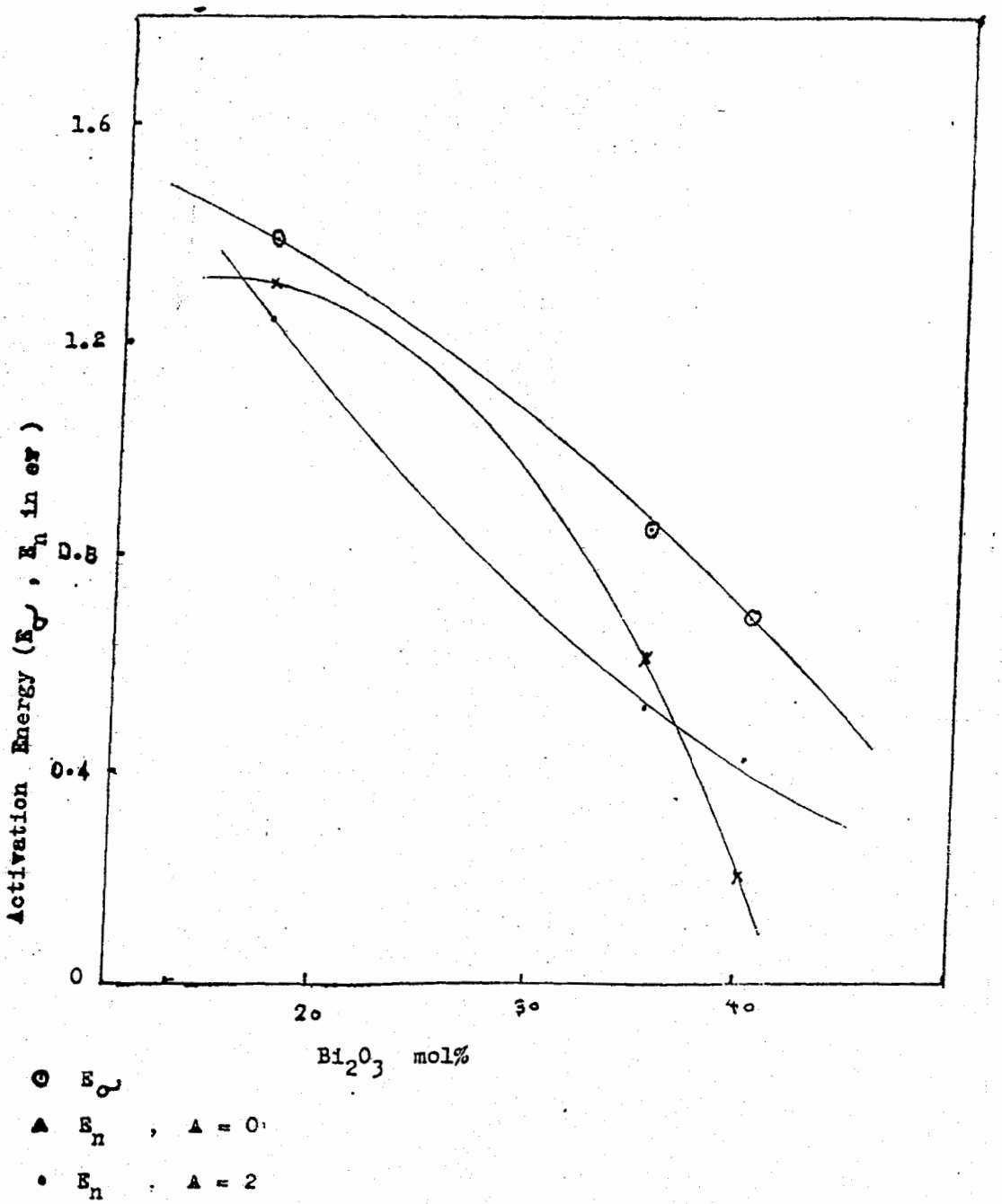

Fig. (4): The dependence of activation energy on the persentage of the presence of Bi_2O_3 in the samples.