Commun. Fac. Sci. Univ. Ank. Series B
V. 39. pp. 45-56 (1993)

# ELECTRICAL AND SPECTROSCOPIC PROPERTIES OF SOME GAMMA - IRRADIATED GLASSES

by

Z.A. EL-HADI

*Chemistry Department, University College For Girls, Ain-Shams University, Heliopols, Cairo, Egypt.*

(Received July, 8, 1992; Accepted Jan. 14, 1993).

ABSTRACT

Electrical conductivity and infrared absorption spectra of some gamma-irradiated sodium borate glasses were studie.d

The raw materials were of chemically pure grade. All melts were made in Pt-Rh crucibles in an electric furnace at a temperature of 1100 'C and the duration of melting was two hours. The molten glasses, after pouring and setting, were annealed.

The experimental results obtained revealed that:

1. The values of the electrical conductivity of the glasses studied increase with the gradual increase of the soda content, gamma-irradiation doses and the temperature which may be due to the formation of the non-bridging oxygen ions, the color centers formation and the increase of the sodium ion mobility, respectively.
2. The intensity of the characteristic infrared absorption bands tends to increase with the increase of either the soda content or the gamma-irradiation doses which may be attributed the increase of the d-p orbital mixing and to the presence of the impurities lr the lattice defects in the glass structure, respectively. The displacement of the absorption bands towards longer wavelentgh with the gradual increase of the soda content may be due to the decrease in the ligand fields strength at the higher soda content.

## INTRODUCTION

The structure of the alkali borate glasses has been the subject of many investigations. Interest in the study of these glasses has been lately renewed, due to the discovery of the glass compositions exhibiting exceptionally high ionic conductivity. Ionic conductivity in solids has been related to the ion migration from one site to a neighboring one(1). Among other factors, the ionic hopping rate between the neighboring sites(2), as well as the activation energy for ionic migration(3), depends on the frequency of the mobile electron vibration. It was concluded that(4) the estimation of the effective ion attempt frequency appeared quite high which was attributed to the possibility that an ion can form more than one jump, depending on the number of the available nei boring sites. Values of the attempt frequencies can be directly obtained from far-infrared measurements, requiring no assumptions to be made or other additional informations. Far-infrared spectra of ionic oxide glasses were initially reported by Exarhos et al(5). It was observed that metal cations in the glass matrices give the characteristic absorption bands in the far-infrared, due to the vibrations of the cations in their network sites. Subsequently, cation-motion bands were observed in the far-infrared spectra of various other glass systems(6) and proved to give valuable informations for understanding the transport and the glass transition phenomena in glasses (3, 7). The binary alkali metal borate glasses are of special interest since they can from the basis for a great variety of fast ionic conducting systems(8). Understanding the ionic conduction process in multicomponent glasses requires good knowledge of the corresponding phenomena in the simpler binary alkali borate glasses(9). The way by which alkali metal ions interact with the borate network is of importance for the ionic transport. Far-infrared spectra of alkali metal boratae glasses can provide useful informations concerning such cation-network interactions. The objective in the present work is to elucidate some conclusions drawn about some binary sodium borate glasses based on electrical and spectroscopic techniques, with the view to throw some light on the structure of these selected glasses and posibly on the glass structure.

## EXPERIMENTAL

Raw materials, melting and preparation of the glass samples:

The chemicals used were of chemically pure grade and were finely pulverised. Boric oxide was introduced in the form of boric acid and soda was introduced in the form of sodium carbonate. All the glass batches were melted in an electric furnace at a temperatire of 1100 'C and the duration of melting was two hours. The molten glasses, after pouring and setting, were annealed.

## IRRADIATION PROCEDURE

The gamma-cell used was 220 canadian type of 6300 curie $Co^{60}$. The total dose was ranging from 60 to 340 k. rad.

Electrical conductivity measurements:

The glass samples used were prepared as a disc ground and polished from the two surfaces, then the disc was fixed to the double electrodes. The disc thickness for each glass sample and the electrode area were measured and calculated at temperature ranging from 40 to 350 °C.

The specific electrical conductivity for each glass sample was calculated by using the following equation:

$$\sigma = \frac{L}{A} \cdot \frac{1}{R_x} \qquad \ldots\ldots \text{ where,}$$

$\sigma$ is the electrical conductivity for each glass sample;

L is the glass sample thickness in cm;

A is the glass sample cross sectional area in $cm^2$; and

$R_x$ is the glass sample resistance.

The activation energy Eg for the glass samples was calculated as follows:

$$\sigma = \sigma_0 \, e^{-Eg/KT} \qquad \ldots\ldots \text{ where,}$$

$\sigma$ is the electrical conductvitiy for the glass sample;

$\sigma_0$ is constant;

E is the activation energy for the glass sample;

K is the Boltzman constant; and

T is the absolute temperature.

Infrared spectrophotometric measurements:

The KBr–technique for the infrared spectroscopy was used. The absorption spectra between about 5000 and 300 $cm^{-1}$ were recorded on a URIO double–beam infrared spectrophotometer. The infrared measurements for all the irradiated glass samples were carried out directly after removal from the gamma–cell within ten minutes.

## RESULTS AND DISCUSSIONS

### *Electrical measurements*

1– Effect of the glass composition:

Electrical measurements at a constant temperature (180 °C) of some sodium borate glasses irradiated to a constant gamma–ray dose (3.4 x $10^5$ rad / hr), were studied. From the experimental results obtained, Table (1) and Fig. (1), it can be seen that the values

Table (1). Chemical compositions and values of electrical conductivity and activation energy of a number of sodium borate glasses irradiated to a constant gamma-irradiation dose ($3.4 \times 10^5$ rad / hr).

| Glass No. | Glass compositions wt % | | Electrical conductivity $-\log \sigma$ | Activation energy Eg |
|---|---|---|---|---|
| | $B_2O_3$ | $Na_2O$ | | |
| 1 | 95 | 5 | 13.40 | 1.0267 |
| 2 | 85 | 15 | 11.75 | 1.0580 |
| 3 | 80 | 20 | 10.65 | 0.9590 |
| 4 | 75 | 25 | 11.25 | 1.0130 |
| 5 | 65 | 35 | 09.50 | 0.8555 |

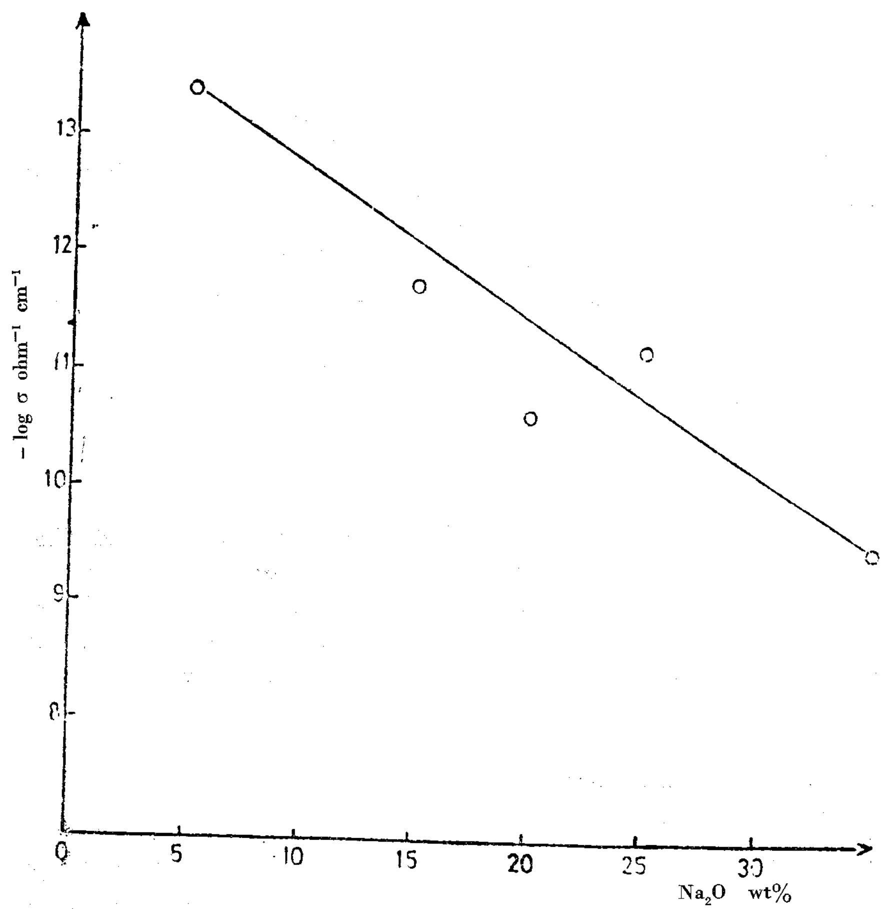


Fig. 1. Electrical conductivity of a number of sodium borate glasses irradiated to a constant gamma-irradiation dose ($3.4 \times 10^5$ rad / hr.).

of the electrical conductivity increase with the gradual increase of the soda content which may be due to the breakdown of the bridging oxygen bonds and the formation of the non–bridging oxygen ions(10); thus open structure is obtained threugh which the charge carriers can move with high mobility11). The decrease in the values of the activation energy with the increase of the soda content in these glasses may be attributed to the coulomb potentials between the cation sites which increase their mutual overlap(12).

2- Effect of the gamma–ray doses:

The effect of increasing the gamma–irradiation doses gradually from 0.6 x $10^5$ to 3.4 x $10^5$ rad / hr on the electrical measurements at a constant temperature (180 °C) of the glass of the base composition $B_2O_3$ 80%, $Na_2O$ 20%, was studied. From the results obtained, Table (2) and Fig. (2), it can be seen that the values of the electrical conductivity tend to increase with the gradual increase of the gamma –irradiation dose while the values of the activation energy decreases which may be attributed to the formation of the color centers and the desrease in the number of the intrinsic defects that have no trapped electrons or holes in the glass network structure(13).

Table (2). Chemical compositions and values of electrical conductivity and activation eneryg of a number of sodium borate glasses of the base composition $B_2O_3$ 80 % $Na_2O$ 20 % irradiated to different gamma–irradiation doses

| | Glass compositions wt % | | Gammairradiation dose rad /hr | Electrical conductivity –log σ | Activation energy Eg |
|---|---|---|---|---|---|
| | $B_2O_3$ | $Na_2O$ | | | |
| 6 | 80 | 20 | 0.60 x $10^5$ | 10.85 | 0.9770 |
| 7 | 80 | 20 | 1.35 x $10^5$ | 10.40 | 0.9366 |
| 8 | 80 | 20 | 2.70 x $10^5$ | 10.80 | 0.9300 |
| 3 | 80 | 20 | 3.40 x $10^5$ | 10.65 | 0.9590 |

3- Effect of the temperature:

The effect of increasing the temperature on the electrical measurements of the glass of the base composition $B_2O_3$ 80%, $Na_2O$ 20%, irradiated to a constant gamma–ray dose (3.4 x $10^5$ rad / hr), was studied. From Fig. (3), it can be seen that the electrical conductivity increases gradually with the gradual increase of temperature which may be due to the increase of the alkali ion mobility(14).

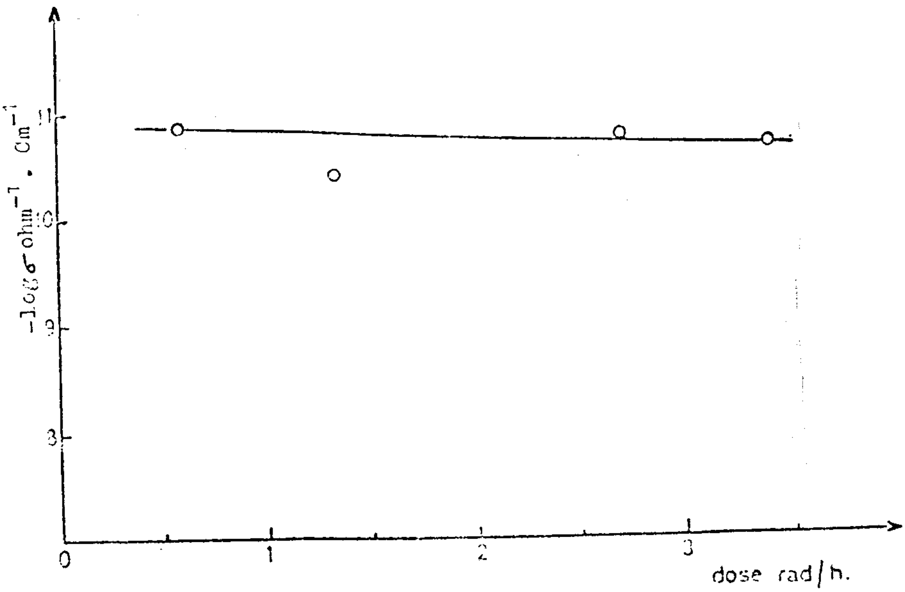


Fig. 2. Electrical conductivity of a sodium borate glass of the base composition $B_2O_3$ 80 %, $Na_1O$ 20 % irradiated to different famma-irradiation doses.

## *Infrared absorption spectra :*

### 1– Effect of the glass composition:

Infrared absorption spectra of some sodium borate glasses, irradiated to a constant gamma-ray dose (3.4 x $10^5$. rad / hr), were studied. The experimental results obtained are given in Table (3) and aie shown in Fig. (4), from which it can be seen that:

Table 3. Chemical compositions and positions of the infrared absorption bands of a number of sodium borate glasses irradiated to a constant gamma-irradiation dose: (3.4 x $10^5$ rad / hr).

| Class No. | Class compositions wt % | | Band 1 $Cm^{-1}$ | Band 2 $Cm^{-1}$ | Band 3 $Cm^{-1}$ | Band 4 $Cm^{-1}$ | Band 5 $Cm^{-1}$ | Band 6 $Cm^{-1}$ | Band 7 $Cm^{-1}$ | Band 8 $Cm^{-1}$ | Band 9 $Cm^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $B_2O_3$ | $Na_2O$ | | | | | | | | | |
| 9 | 95 | 5 | 3320 | 1410 | 1355 | 1195 | 1096 | 940 | 790 | 750 | — |
| 10 | 85 | 15 | 3310 | 1405 | 1358 | 1158 | 1085 | 930 | 780 | 700 | — |
| 11 | 80 | 20 | 3300 | 1400 | 1350 | 1190 | 1090 | 925 | 785 | 700 | — |
| 12 | 75 | 25 | 3200 | 1390 | 1340 | 1180 | 1080 | 915 | 750 | 690 | — |
| 13 | 65 | 35 | 3200 | 1380 | 1345 | 1180 | 1080 | 915 | 750 | 690 | 505 |

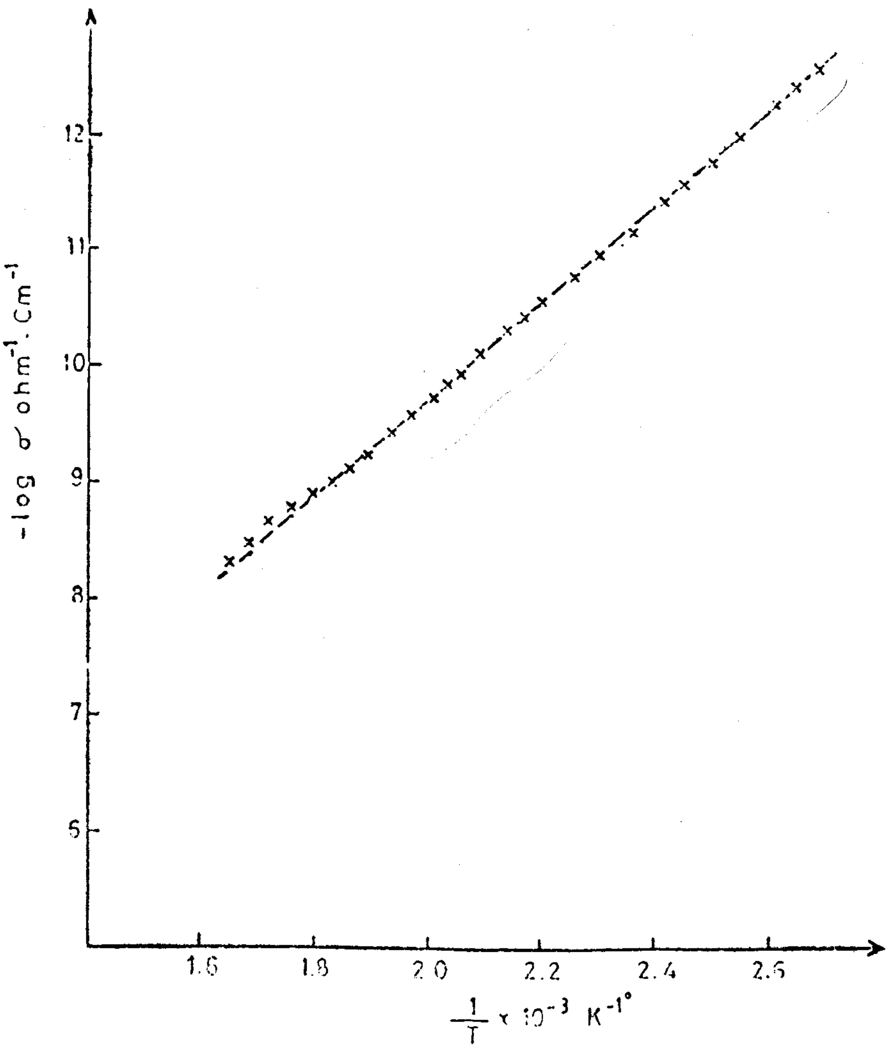


**Fig. 3. Electrical conductivity of a sodium borate glass of the base composition $B_2O_3$ 80 %, $Na_2O$ 20 % irradiated to a constant gamma-irradiation dose (3.4 x $10^5$ rad / hr.) for different temperatures.**

Eight absorption bands at 3320, 1410, 1355, 1195, 1095, 940, 790 and 750 $cm^{-1}$ were observed in the absorption spectra given by the glass of the composition $B_2O_3$ 95%, $Na_2O$ 5%, which may be attributed to O-H stretching vibrations, stretching vibrations of the boroxal ring, some triangle boron changed to tetrahedra to form diborate, antisymmetric stretching vibrations involving bridging

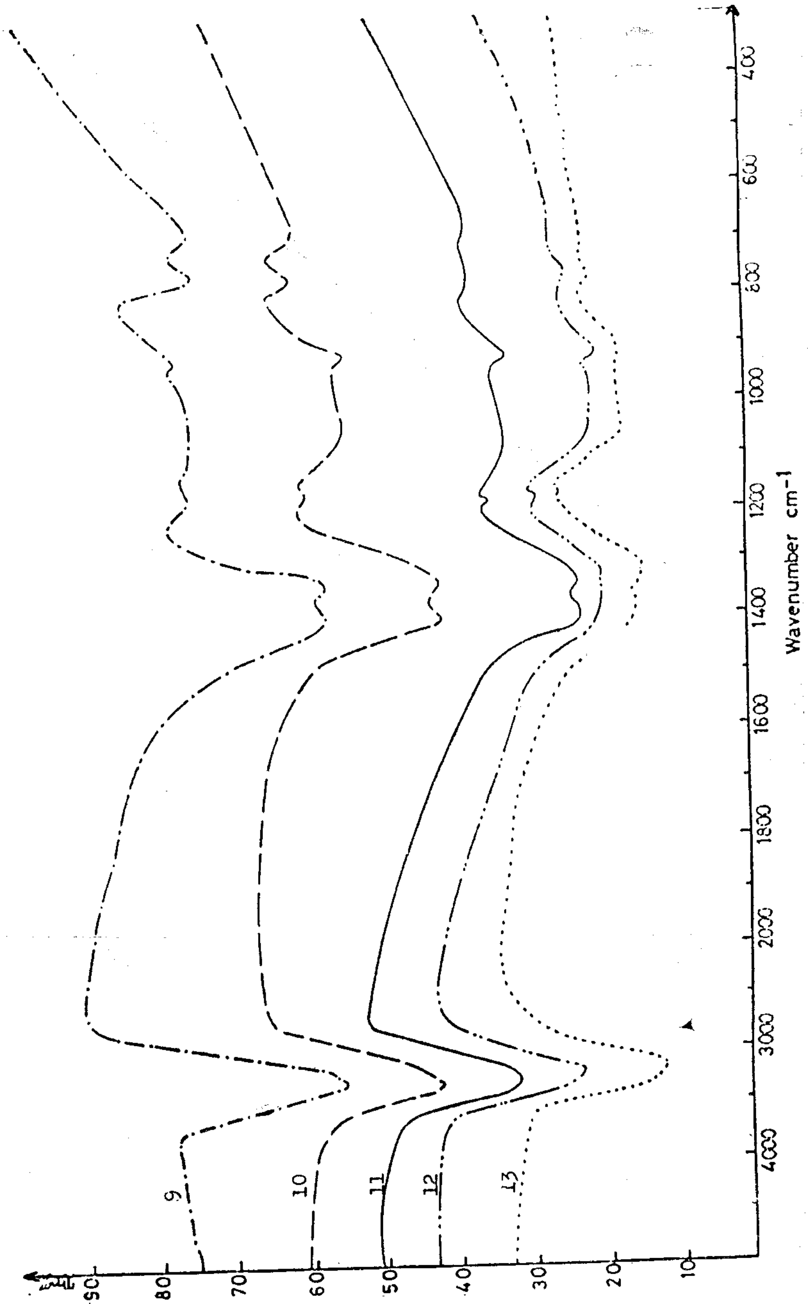


Fig. 4. Infrared absorption spectra of a number of sodium borate glasses irradiatied to a constant gamma-irradiation dose (3.4 x $10^5$ rad / h).

oxygens, $BO_4$ vibrations, B–O linkages of $BO_4$ groups, stretching vibrations of the non-bridging oxygens and B–O–B vibrations, respectively(15).

The progressive increase of the soda content caused, in principle, the following changes:

i. The positions of the absorption bands at 3320, 1410, 1355, 1195, 1095, 940, 790 and 750 $cm^{-1}$ in the glass of the composition $B_2O_3$ 95%, $Na_2O$ 5%, changed to 3200, 1380, 1345, 1180, 1080, 915, 750 and 690 $cm^{-1}$ in the glass of the composition $B_2O_3$ 65%, $Na_2O$ 35% respectively, which may be due to that the higher soda content implies a decrease in the ligand field strength and hence the displacement towards longer wavelengths takes place(16).

ii. A new absorption band at 505 $cm^{-1}$ was observed in the absorption spectra given by the glass of the composition $B_2O_3$ 65%, $Na_2O$ 34% which may be due to the motion of the alkali ion in the glassy network.

iii. The values of the optical density of all the absorption bands increased with the gradual increase in the soda content, which may be arise from the increased d–p orbital mixing related presumably to the lower ligand field strength at the higher alkali content(16).

2– Effect of the gamma–ray doses:

Effect of increasing the gamma–irradiation dose on the infrated absorption spectra given by the glass of the base composition $B_2O_3$ 80%, $Na_2O$ 20% exposed to different doses $1.35 \times 10^5$ and $3.4 \times 10^5$ rad / hr respectively, was studied. The results obtained, Table (4) and Fig. (5), revealed that the positions of the infrared absorp-

Table 4. Cçemical compositions and positions of the infrarred absorption bands of a number of sodium borate glasses of the base composition $B_2O_3$ 80 %, $Na_2O$ 20 % irradiated to different gamma–irradiasiton doses.

| Glass No. | Class compositions wt % | | Gammair-radiation dose rad / hr | Band 1 $Cm^{-1}$ | Band 2 $Cm^{-1}$ | Band 3 $Cm^{-1}$ | Band 4 $Cm^{-1}$ | Band 5 $Cm^{-1}$ | Band 6 $Cm^{-1}$ | Band 7 $Cm^{-1}$ | Band 8 $Cm^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $B_2O_3$ | $Na_2O$ | | | | | | | | | |
| 14 | 80 | 20 | $1.35 \times 10^5$ | 3300 | 1400 | 1350 | 1190 | 1095 | 940 | 790 | 750 |
| 11 | 80 | 20 | $3.4 \times 10^5$ | 3300 | 1400 | 1350 | 1190 | 1095 | 940 | 790 | 750 |

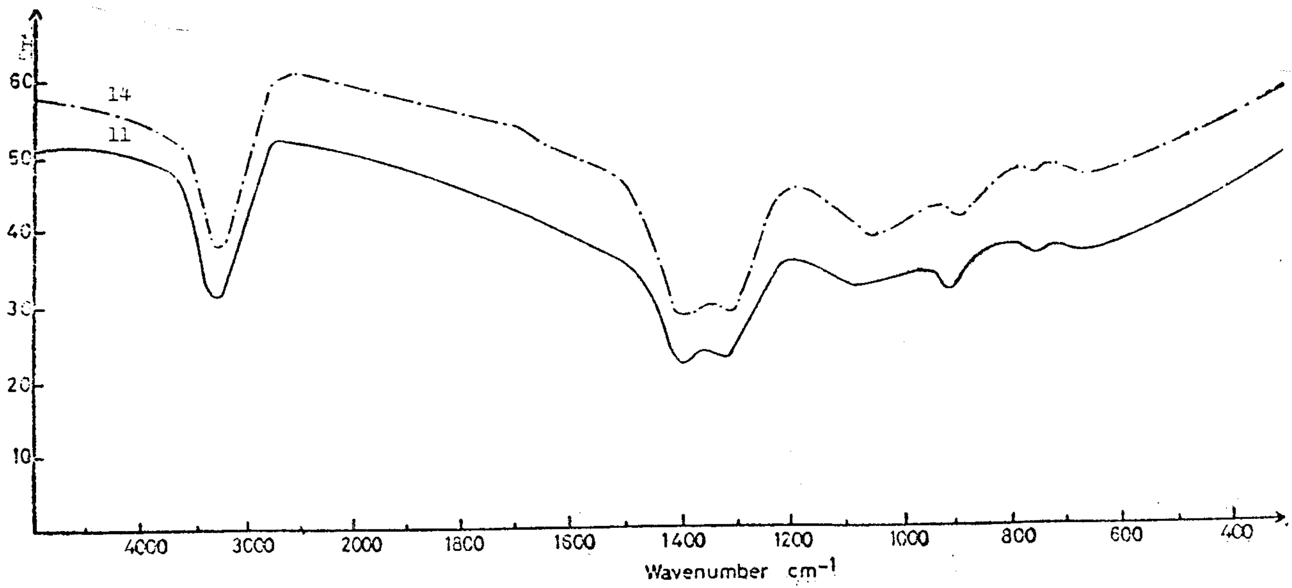


Fig. 5. Infrared absorption spectra of a sodium borate glass of the base composition $B_2O_3$ 80 %, $Na_2O$ 20 % irradiated to different gamma-irradiation doses.

tion bands at 3300, 1400, 1350, 1190, 1090, 925, 785 and 700 $cm^{-1}$ were not affected, while the values of the optical density of all these absorption bands increased with the increase of the gamma-irradiation dose. Generally, this increase can be related to the presence of the lattice defects and impurities in the glass before the irradiation. As the glass is irradiated, the color centers are formed by trapping electrons or holes. The number of the intrinsic defects that have no trapped electrons or holes decreases with increasing gamma-ray dose. Therefore, the increase in the values of the optical density is expected to take place (17-20).

## REFERENCES


1. KAMITSOS, E.I., KARAKASSIDES, M.A. and CHRYSSIKOS, G.D., J. Phys. Chem. 91, 5807, 1987.
2. MEGEEHIN, P. and HOOPER, A., J. Mater. Sci., 12, 1, 1977.
3. EXARHOS, G.J., MILLER, P.J. and RISEN, W.M. Jr., Solid State Commun, 17, 29, 1975.
4. a. ALMOND, D.P. and WEST, A.R., Solid State Ionics; 9 / 10, 277, 1983.

   b. MUNDY, J.N. and JIN, G.L., Solid State Ionics; 21, 303, 1986.
5. EXARHOS, G.J. and RISEN, W.M. Jr., Shem. Phys. Lett.; 10, 484, 1971.
6. a. PAEGLIS, A.U., Ph. D. Thesis, Brown University, 1979.

   b. WINDISCH, C.F., Ph. D. Thesis, Brown University, 1982.

   c. ROA, C.N.R., RANDHAWA, H.S., REDDY, N.V.R. and CHAKRAVARTY, D., Spectrochim. Acta, Part A, 1975, 31 A, 1283.

   d. NELSIN, B.N. and EXARHOS, G.J., J. Chem. Phys., 71, 2739, 1979.
7. EXARHOS, G.J., MILLER, P.J. and RISEN, W.M., J. Chem. Phys. 60, 4145, 1974.
8. TULLER, H.L., BUTTON, D.P. and UHLMANA, D.R., J. Non-Cryst. Solids, 40, 93, 1980.
9. KAMITSOS, E.I., KARAKASSIDES, M.A. and CHRYSSIKES, G.D., J. Phys. Chem., 90, 4528, 1986.
10. OWEN, A.E., Progress in Ceramic Sci., 7, 77, Oxford, Pergamon, 1963.
11. ABO-ZEID, Y.M., Ph. D. Thesis, Al-Azhar University, Cairo, Egypt, 1990.
12. STEVE, W.M., J. Amer. Ceram. Soc., 71, 6, 438, 1988.
13. MOUSTAFFA, F.A., GHONEIM, N.A., ZAHRAN, A.H. and EZZ EL-DIN, F.M., Non-Cryst. Solids, 55, 3553, 1983.
14. KINSER, D.L., and HENCH, L.L., J. Amer. Ceram. Soc., 51, 8, 1968.
15. a. GADSDEN, J.A., Infrared Spectra of Mineral and Related Inorganic Compounds,

The Butter Worth, London, 1975.

b. KROGH-MOE., J. Phys. Chem. Glasses, 6, 46, 1965.

c. IRION, M. and COUZI, M., J. Solid State Chem., 31, 285, 1980.

d. TENNEY, A.S. and WONG, J., J. Chem. Phys., 56, 1976.

e. VONG, J. and ANGELL, C.V., Spectroscopy of Gass, 1976.

16. BAMFORD, C.R., Phys. Chem. Classes, 3, 6, 189, 1962.

17. LELL, E., KREIDL, N.J. and HENSLER, J.R., Progress in Ceramic Sci., Vol. 4 (Pergamon Press), N.Y., 1, 1966.

18. BISHAY, A., J. Non-Cryst. Solids, 3, 54, 1970.

19. FRIEBELE, E.J. and GRISCOM, D.L., Treatise on Materials Sci. and Tech., Vol. 17, ads. M. Tomozawa, R.H. Doremus (Academic Press), N.Y., 257, 1979.

20. RAO, K.J., ELLIOC, S.R., J. Non-Cryst. Solids, 46, 371, 1981.