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# Infrared study of the effect of heat treatment and irradiation on barium borate glass containing iron

A. M. SANAD, I. KASHIF, A. A. EL-SHARKAWY, A. A. EL-SAGHIER, H. FAROUK
*Physics Department, Faculty of Science, Al-Azhar University, Nasr-City, Cairo, Egypt*

A barium borate glass system was prepared containing different amounts of iron. The prepared glasses were heat treated at 550° C for 2, 6, 12, 18 and 24 h. Also the glasses were irradiated using $\gamma$-ray at a dose of $4.805 \times 10^4$ rad h$^{-1}$ for 12, 18 and 24 h. The infrared spectra were recorded for the untreated and heat treated samples. It was found that, when the $Fe_2O_3$ was introduced in the glass the triangle $BO_3$ groups were transferred to $BO_4$ groups. The formation of non-bridging oxygen with high concentration was also observed as a result of introducing $Fe_2O_3$ in the glass. The absorption bands of the IR spectra of the irradiated samples indicated no significant variations, and only a transfer of some $BO_4$ groups to $BO_3$ groups could be observed.

## 1. Introduction

The specific changes produced when a glass system is subjected to heat treatment have been shown to depend not only on the heat treatment temperature but also on the time of heat treatment. Rawson [1] studied the phase separation in binary barium borate glass system. Fahmy *et al.* [2–4] studied the effect of nucleating agents on the crystallization process of $BaO-B_2O_3$ glass system. Bagomolova *et al.* [5] studied the effect of irradiation in EPR and optical spectra of sodium-silicate, sodium-borate and sodium-phosphate glasses.

The present work includes the study of the effect of the time of heat treatment and irradiation on the molecular structure of barium borate glasses containing $Fe_2O_3$. The change in molecular structure was determined by studying the corresponding changes in the infrared spectra of the heat treated and irradiated samples.

## 2. Experimental details

Powders of pure chemicals over 98.5% purity were thoroughly mixed together into a homogeneous mixture. The homogeneous mixture was melted in an electric furnace at 1100° C for 2 h and then quenched in air to prepare a glass system according to the molar formula, 75 mol % $B_2O_3$–$(25-x)$ mol % BaO–$x$ mol % $Fe_2O_3$, where $x$ = O, 1, 2.5, 7.5 and 10. The glass samples obtained were heat treated at 550° C for 2, 6, 12, 18 and 24 h. The samples were also irradiated for 12, 18 and 24 h using $\gamma$-ray at a dose of $4.805 \times 10^4$ rad h$^{-1}$. The samples were crushed into powder form and examined for molecular structure variation by IR technique. The IR spectra were recorded on DIGILAB FTS 20C infrared spectrophotometer.

## 3. Results and discussion

### 3.1. Effect of heat treatment

The infrared spectra of the glasses under investigation have been recorded in the region between 400 to 4000 cm$^{-1}$ in order to obtain information about the change in vibrational spectra due to process of co-ordination variations.

The infrared spectra of borate glasses showed three principal bands at 700, 1260 and at 1420 cm$^{-1}$. The band at 700 cm$^{-1}$ is due to $>B–O–B<$ vibration [6], while the other two bands are due to $>B–O–\overset{|}{\underset{|}{B}}–$ vibration [7, 8].

Since the addition of BaO to the binary borate glass gives an extra oxygen atom which is accommodated in the network, a transfer of some boron atoms from triangle $BO_3$ to $BO_4$ occurs. This could be deduced from the shift of the band at 1420 cm$^{-1}$ to lower frequency. Also the vibration of some boron atoms which are attached to non-bridging oxygen in the form $>B–O^-$ or $B–O–B<O^-$ appeared as a new band at 1010 cm$^{-1}$ [9].

The IR spectrum of the untreated 25 BaO–75 $B_2O_3$ glass sample, Fig. 1, shows four bands at 695, 1025, 1240 and at 1400 cm$^{-1}$. These bands indicate the presence of $BO_3$, $BO_4$ and non-bridging oxygen in the form of tetraborate and diborate groups [10]. Infrared spectra of the untreated samples containing $Fe_2O_3$ with different contents, Fig. 1, shows that the introduction of $Fe_2O_3$ to the glass batches caused a slight shift in the positions of the first two bands to be at 700 and 1010 cm$^{-1}$. Also as a result of the introduction of $Fe_2O_3$ in increasing amounts, the intensities of the bands at 700 and 1010 cm$^{-1}$ were decreased while the intensity of the band at 1400 cm$^{-1}$ was increased, this was observed at the concentration of 1 mol % $Fe_2O_3$

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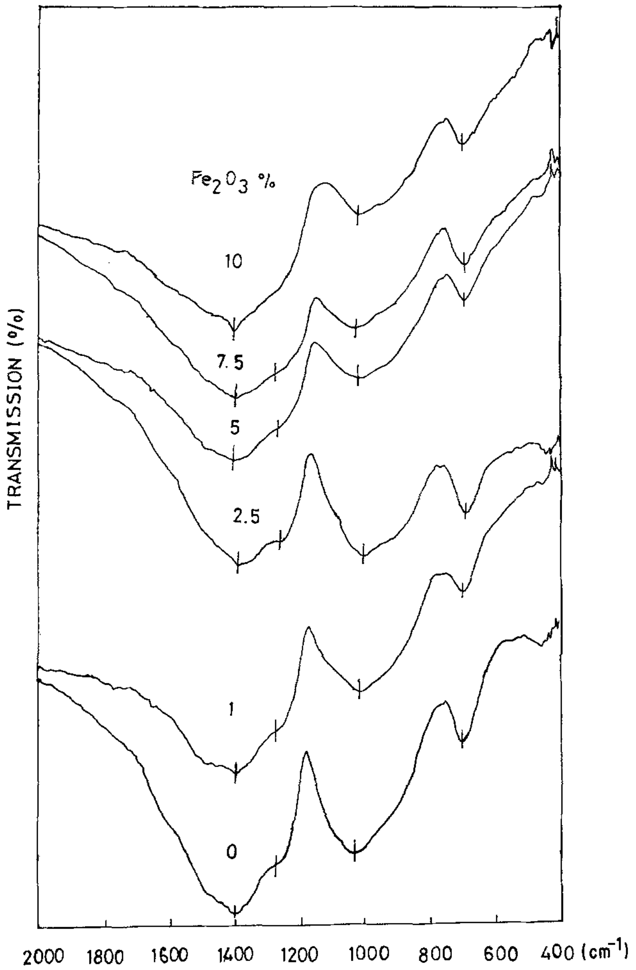

*Figure 1* Infrared spectra of 75 mol % $B_2O_3$–(25–$x$) mol % BaO–$x$ mol % $Fe_2O_3$ glass system.

(Table I). At 2.5 mol % $Fe_2O_3$ concentration an increase in the intensities of the bands at 700 and $1010\,cm^{-1}$ was found, while the intensities of the three mentioned bands were found to decrease in all samples containing more than 2.5 mol % $Fe_2O_3$ except the intensity of the band at $1400\,cm^{-1}$ which was found to increase again in the sample containing 10 mol % $Fe_2O_3$.

The infrared spectra of heat treated samples for 2 h, Fig. 2, shows the above four mentioned bands in addition to two bands at 1080 and $1100\,cm^{-1}$ observed only in the spectrum of the sample containing 10 mol % $Fe_2O_3$. First band at $1080\,cm^{-1}$ which is due to transfer of some boron triangle to boron tetrahedra vibration. Band at $1100\,cm^{-1}$ is due to the presence of non-bridging oxygen in form of $>B–O^-$ vibration [8].

In the spectra of heat treated samples for 6 h the bands at 1010 and at $1400\,cm^{-1}$ disappeared completely. This means that the boron in these samples are in the form of boron triangle $BO_3$ only. New band at $465\,cm^{-1}$ was observed in sample containing 1 and 2.5 mol % $Fe_2O_3$. In addition to the band at $465\,cm^{-1}$ another band at $550\,cm^{-1}$ was observed in the spectrum of sample containing 10 mol % $Fe_2O_3$, Fig. 3, these two bands are due to $Fe_3O_4$ group vibration [11].

In the IR spectra of the heat treated samples for 12 h, Fig. 4, the four principal bands at 695, 1020, 1200 and $1400\,cm^{-1}$ were observed in the spectra of samples containing 7.5 and 10 mol % $Fe_2O_3$, while no bands except only one band at $700\,cm^{-1}$ was observed in the spectra of the samples containing iron oxide less than 7.5 mol %. This indicates the presence of both the non-bridging oxygen and the $BO_3$ groups.

The same result was obtained from the IR spectra of the heat treated samples for 18 h as that obtained from the spectra of the heat treated samples for 12 h, Fig. 5.

The IR spectra of the sample free from iron and the sample containing 5 mol % $Fe_2O_3$ heat treated for 24 h, Fig. 6, show the four principal bands at 700, 1265 and at $1010\,cm^{-1}$. The fourth band at $1400\,cm^{-1}$ was shifted to lower frequency at $1375\,cm^{-1}$. This indicates that some boron triangle $BO_3$ transfer into boron tetrahedra $BO_4$ forming diborate [12]. While the IR spectra of the samples containing 7.5 and 10 mol % $Fe_2O_3$ heat treated for 24 h, Fig. 6, show the presence of six bands at 470, 540, 700, 1010 and at $1400\,cm^{-1}$. The bands at 470 and $540\,cm^{-1}$ are characteristic for the $Fe_3O_4$ group vibration. The IR spectra of the samples containing less than 5 mol % $Fe_2O_3$ heat treated for 24 h, Fig. 6, show no absorption band except only one band at $700\,cm^{-1}$ which indicates the presence of the boron atoms in triangle form.

The effect of heat treatment on the absorbance and the intensity of the principal bands are summarized in Table I.

## 3.2. Effect of irradiation

Figs 7, 8 and 9 show the IR spectra of the irradiated barium borate and barium borate glasses containing iron up to 10 mol % $Fe_2O_3$. The principal bands which were observed in barium borate glass are shifted to 700, 1010 and $1375\,cm^{-1}$ when irradiated using $\gamma$-ray at a dose of $4.805\,rad\,h^{-1}$ for 12, 18 and 24 h. While the bands in the spectra of barium borate glasses containing iron are shifted to 700, 1050 and $1375\,cm^{-1}$ when irradiated with the same dose for the same time. This indicates the transfer of some boron from $BO_4$ to $BO_3$, while the increase of the irradiation doses leads to the break of the B–O forming non-bridging oxygen.

From the results and the discussion of the effect of the time of heat treatment and the irradiation with different doses it can be concluded that,

(a) The increase in $Fe_2O_3$ content in glass enhances the transformation of boron triangle $BO_3$ to boron tetrahedra $BO_4$ group. This is because the addition of $Fe_2O_3$ on the expense of BaO increases the number of oxygen in the network [13].

(b) The presence of the boron atoms in some samples (with different concentration of $Fe_2O_3$ and heat treated for different times) in the triangle state $BO_3$ may be due to the effect of heat treatment which breaks the B–O bond to form non-bridging oxygen.

(c) The presence of the characteristic bands of $Fe_3O_4$ in the IR spectra of the samples containing more than 5 mol % $Fe_2O_3$ group vibration can be understood on the fact that the iron oxide acts as a glass modifier at a low concentration while at high concentration acts as a former [14].

(d) The IR spectra of the glasses irradiated with different doses show the transformation of some $BO_4$

TABLE I The relation between time of heat treatment and absorbance and intensity of bands

| $Fe_2O_3$ (%) | Time of heat treatment at 550° C (h) | at 700 $cm^{-1}$ | | at 1010 $cm^{-1}$ | | at 1400 $cm^{-1}$ | |
|---|---|---|---|---|---|---|---|
| | | A* | I† | A | I | A | I |
| Zero | Untreated | 0.124 | 0.211 | 0.445 | 2.939 | 0.336 | 0.302 |
| | 2 | 0.088 | 0.141 | 0.342 | 2.397 | 0.301 | 0.512 |
| | 6 | 0.192 | 0.403 | – | – | – | – |
| | 12 | 0.079 | 0.135 | 0.345 | 2.277 | 0.452 | 1.176 |
| | 18 | | | | | | |
| | 24 | 0.234 | 0.398 | 0.720 | 5.401 | 0.234 | 0.468 |
| 1 | Untreated | 0.077 | 0.138 | 0.282 | 1.833 | 0.426 | 1.437 |
| | 2 | 0.112 | 0.199 | 0.347 | 2.219 | 0.234 | 0.734 |
| | 6 | 0.249 | 0.472 | 0.649 | 4.542 | 0.269 | 3.862 |
| | 12 | 0.058 | 0.092 | – | – | – | – |
| | 18 | 0.211 | 0.485 | – | – | – | – |
| | 24 | 0.237 | 0.475 | – | – | – | – |
| 2.5 | Untreated | 0.271 | 0.515 | 0.821 | 5.169 | 0.553 | 1.437 |
| | 2 | 0.113 | 0.215 | 0.328 | 2.065 | 0.564 | 0.736 |
| | 6 | 0.321 | 0.675 | 0.508 | 3.862 | – | – |
| | 12 | 0.125 | 0.287 | – | – | – | – |
| | 18 | 0.196 | 0.412 | – | – | – | – |
| | 24 | 0.214 | 0.428 | – | – | – | – |
| 5 | Untreated | 0.086 | 0.164 | 0.199 | 1.192 | 0.226 | 0.543 |
| | 2 | 0.096 | 0.172 | 0.199 | 1.214 | 0.222 | 0.133 |
| | 6 | 0.230 | 0.484 | – | – | – | – |
| | 12 | 0.357 | 0.713 | – | – | – | – |
| | 18 | 0.301 | 0.512 | – | – | – | – |
| | 24 | 0.209 | 0.355 | 0.426 | 2.684 | 0.301 | 0.587 |
| 7.5 | Untreated | 0.072 | 0.136 | 0.213 | 1.193 | 0.263 | 0.263 |
| | 2 | 0.119 | 0.238 | 0.180 | 1.097 | 0.196 | 0.275 |
| | 6 | 0.220 | 0.353 | 0.388 | 2.64 | 0.368 | 0.626 |
| | 12 | 0.151 | 0.303 | – | – | – | – |
| | 18 | 0.293 | 0.498 | – | – | 0.234 | 0.632 |
| | 24 | 0.183 | 0.300 | 0.392 | 2.428 | 0.385 | 0.501 |
| 10 | Untreated | 0.073 | 0.133 | 0.154 | 0.770 | 0.501 | 0.300 |
| | 2 | 0.064 | 0.135 | 0.026 | – | 0.078 | 0.060 |
| | 6 | 1.657 | 2.485 | 0.370 | 2.330 | 0.376 | 0.639 |
| | 12 | 0.189 | 0.283 | 0.352 | 2.113 | 0.243 | 0.437 |
| | 18 | 0.194 | 0.281 | 0.351 | 2.141 | 0.398 | 0.716 |
| | 24 | 0.301 | – | 0.222 | – | 0.398 | 0.512 |

*A = Absorbance.
†I = Intensity.

TABLE II The relation between time of irradiation and absorbance and intensity of bands

| $Fe_2O_3$ (%) | Time of irradiation (h) | at 700 $cm^{-1}$ | | at 1010 $cm^{-1}$ | | at 1400 $cm^{-1}$ | |
|---|---|---|---|---|---|---|---|
| | | A | I | A | I | A | I |
| Zero | 12 | 0.278 | 0.555 | 0.934 | 6.355 | 0.602 | 0.843 |
| | 18 | 0.288 | 0.605 | 0.806 | 5.160 | 0.477 | 0.716 |
| | 24 | 0.289 | 0.579 | 0.924 | 6.378 | 0.699 | 1.468 |
| 1 | 12 | 0.260 | 0.520 | 0.885 | 6.192 | 0.477 | 0.543 |
| | 18 | 0.232 | 0.440 | 0.813 | 5.284 | 0.778 | 1.012 |
| | 24 | 0.260 | 0.572 | 0.1981 | 6.573 | 0.602 | 0.662 |
| 2.5 | 12 | 0.256 | 0.487 | 0.778 | 5.058 | 0.602 | 0.602 |
| | 18 | 0.245 | 0.442 | 0.699 | 4.543 | 0.778 | 1.089 |
| | 24 | 0.330 | 0.628 | 0.747 | 4.705 | 0.903 | 1.806 |
| 5 | 12 | 0.271 | 0.489 | 0.554 | 3.658 | 0.477 | 0.525 |
| | 18 | 0.373 | 0.746 | 0.632 | 4.235 | 0.699 | |
| | 24 | 0.265 | 0.503 | 0.518 | 3.365 | 0.699 | 0.629 |
| 7.5 | 12 | 0.266 | 0.505 | 0.469 | 2.858 | 0.477 | 0.668 |
| | 18 | 0.359 | 0.718 | 0.564 | 3.781 | 0.602 | 0.662 |
| | 24 | 0.344 | 0.653 | 0.490 | 3.088 | 0.602 | 0.843 |
| 10 | 12 | 0.325 | 0.618 | 0.437 | 2.707 | 0.602 | 0.722 |
| | 18 | 0.382 | 0.763 | 0.531 | 3.455 | 0.477 | 0.525 |
| | 24 | 0.169 | 0.355 | 0.237 | 1.351 | 0.497 | 1.144 |

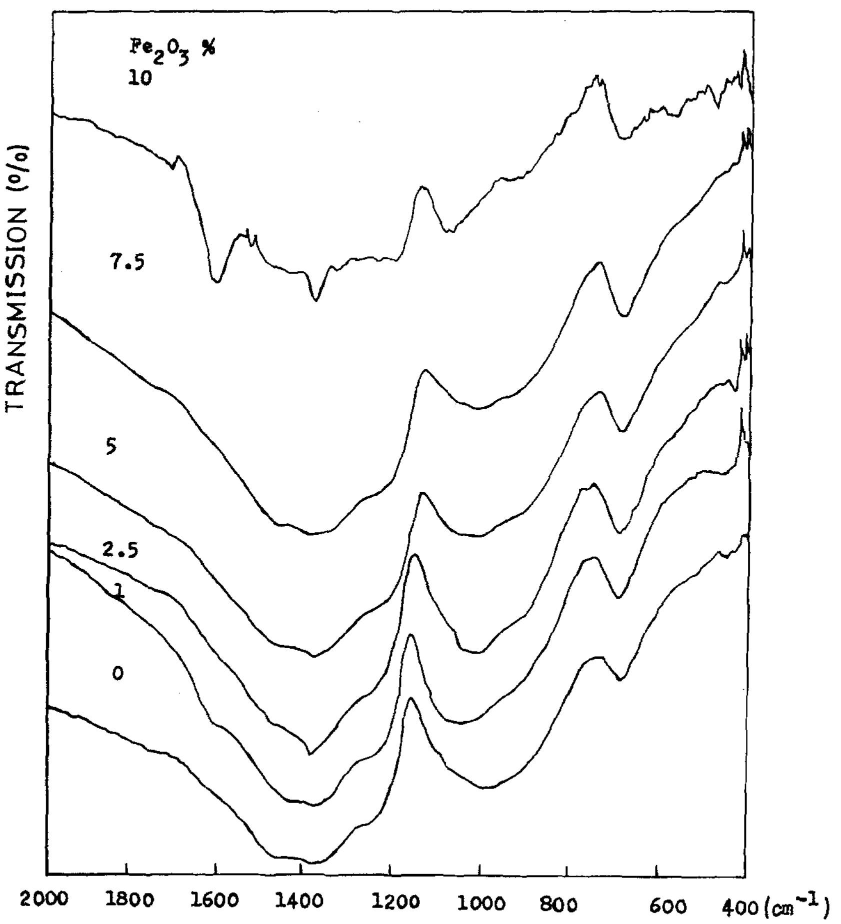

*Figure 2* Infrared spectra of the heat treated samples for 2 h.

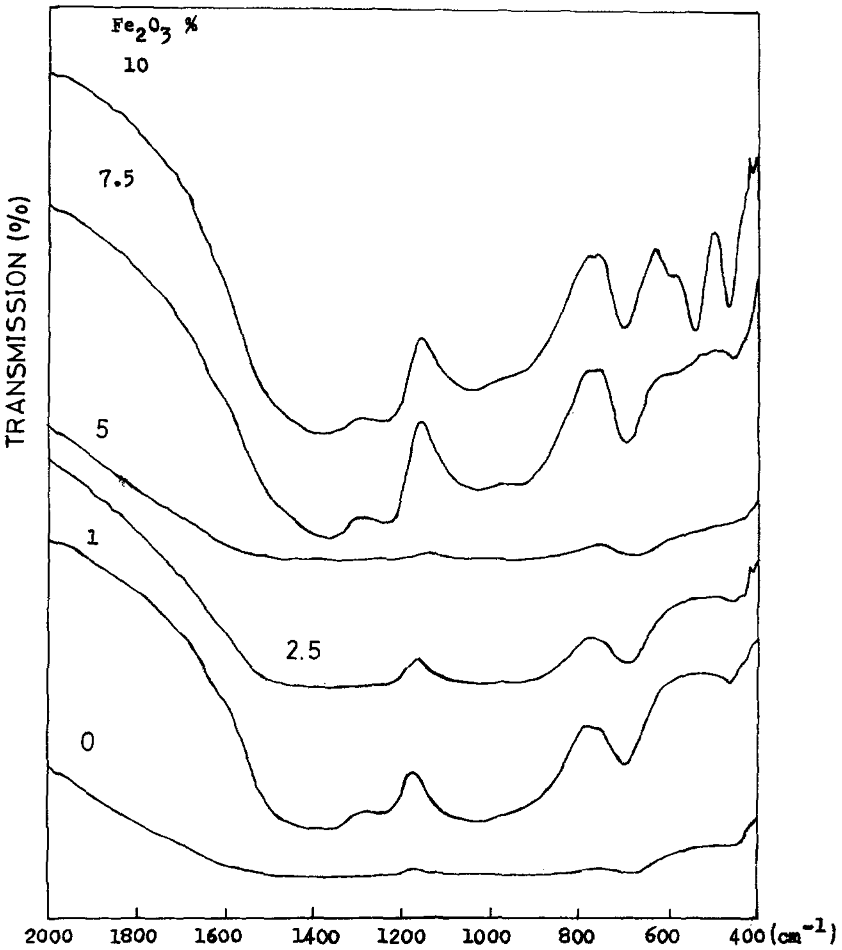

*Figure 3* Infrared spectra of the heat treated samples for 6 h.

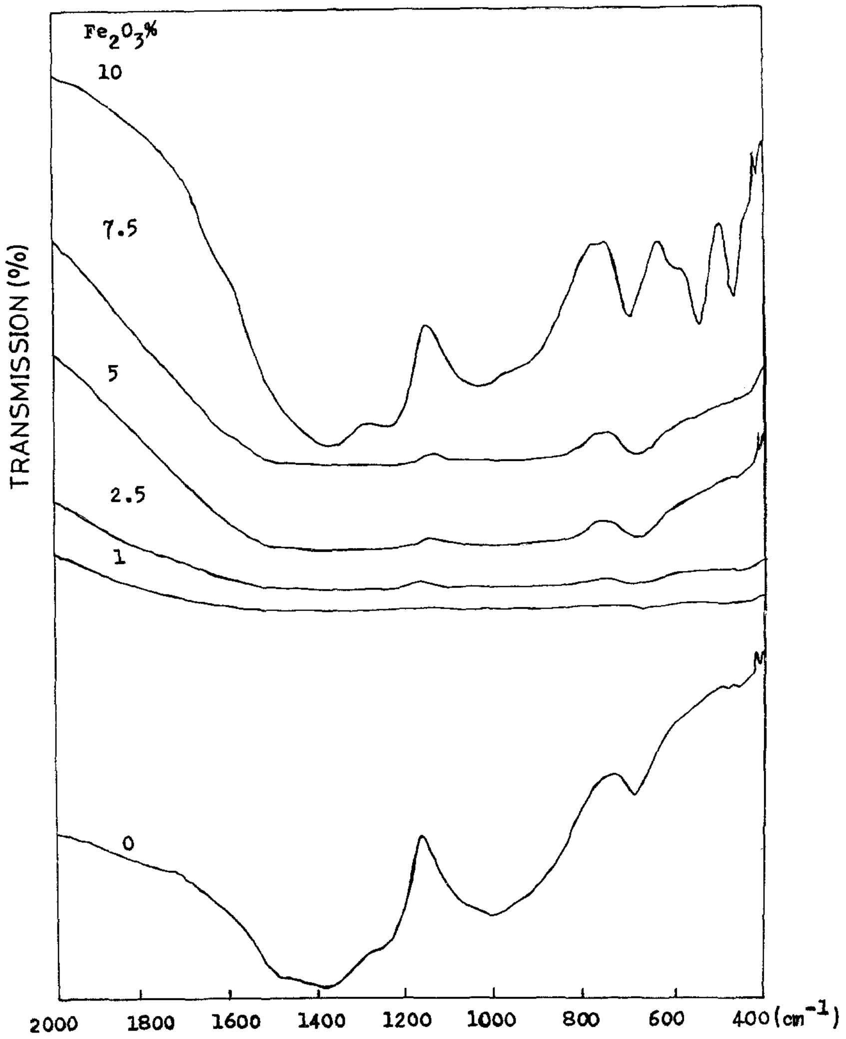

*Figure 4* Infrared spectra of the heat treated samples for 12 h.

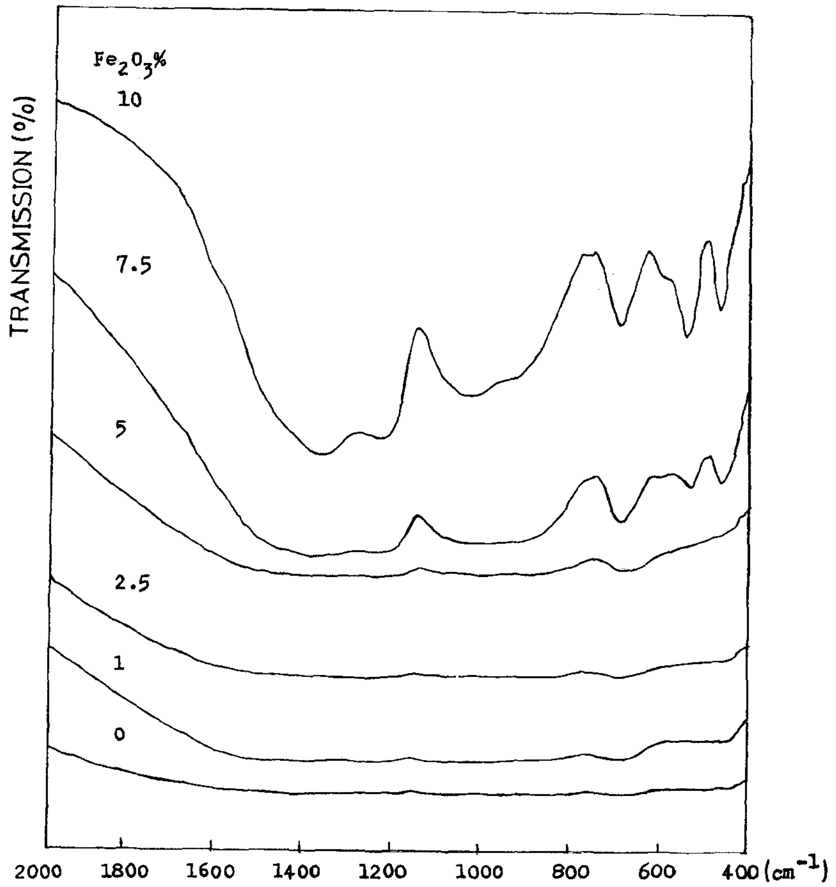

*Figure 5* Infrared spectra of the heat treated samples for 18 h.

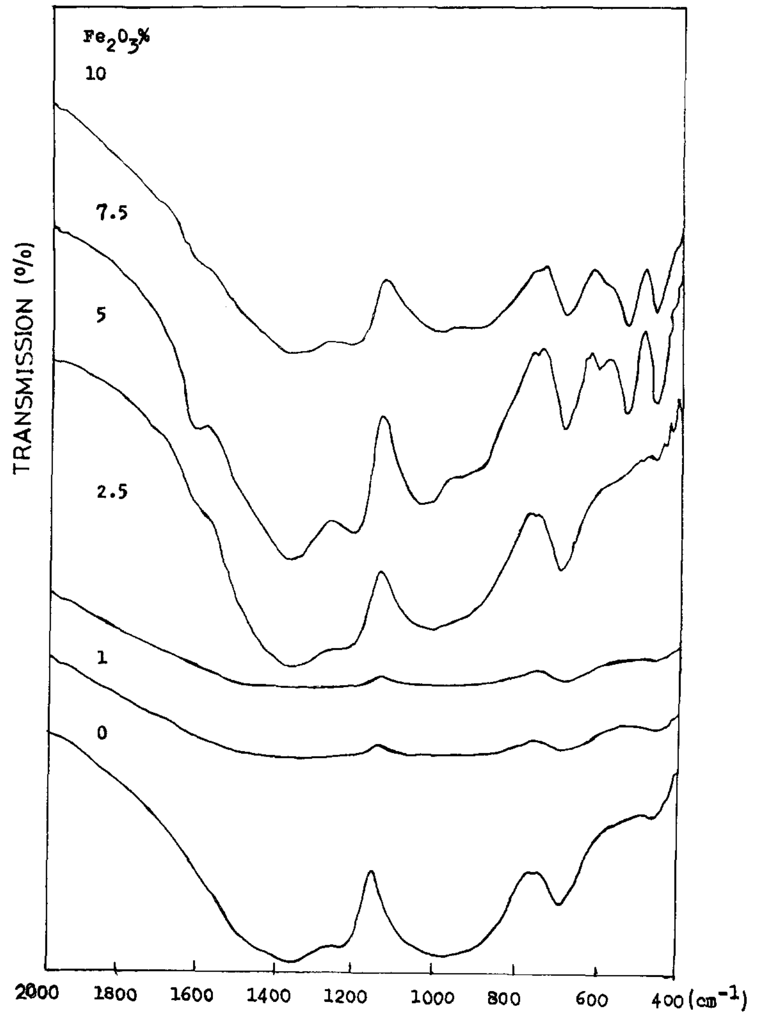

*Figure 6* Infrared spectra of the heat treated samples for 24 h.

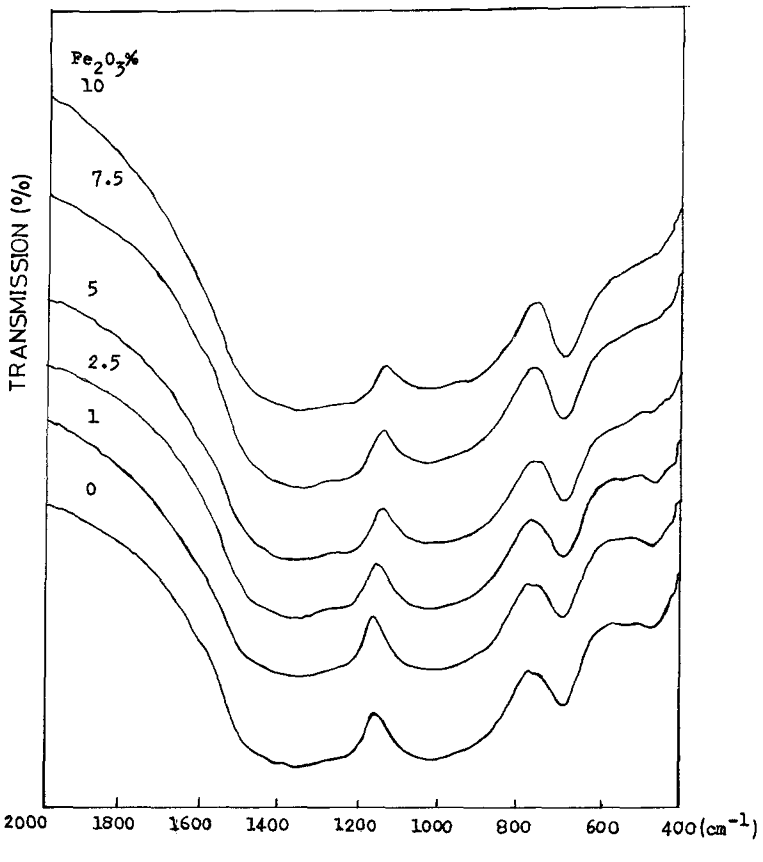

*Figure 7* Infrared spectra of the samples irradiated using $\gamma$-ray for 12 h.

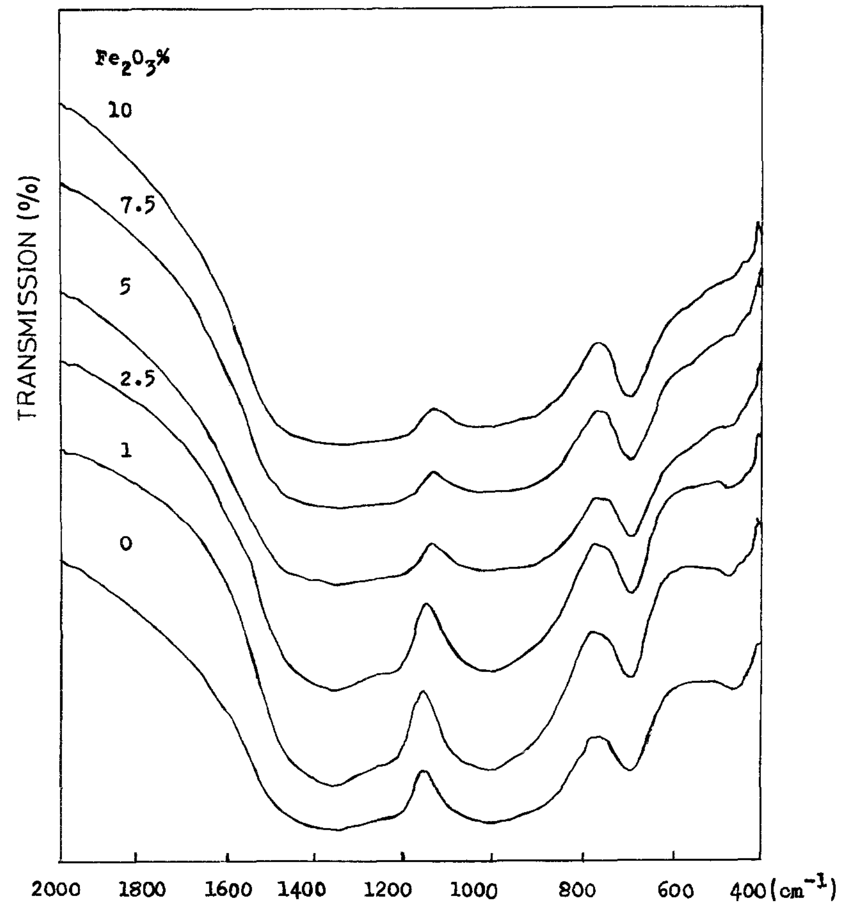

*Figure 8* Infrared spectra of the samples irradiated using γ-ray for 18 h.

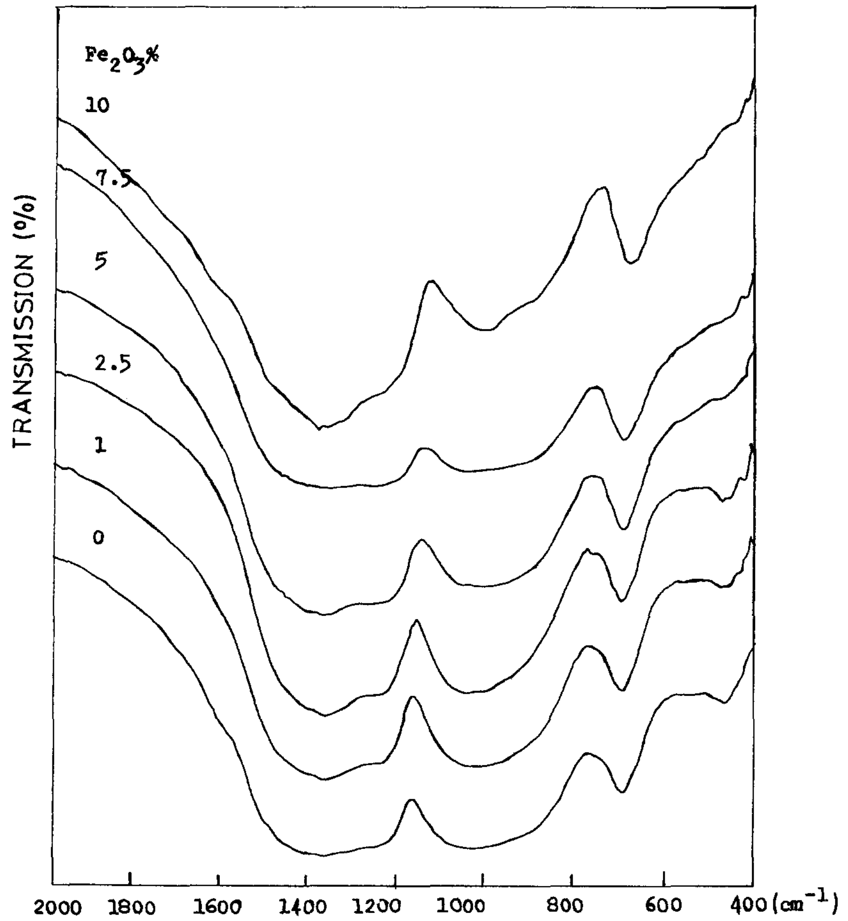

*Figure 9* Infrared spectra of the samples irradiated using γ-ray for 24 h.

to $BO_3$ and the breakage of the B–O bond to form non-bridging oxygen. This observation seems to be independent on the given doses.

## References

1. H. RAWSON, in "Inorganic Glass Forming System" (Academic Press, London, 1967) p. 102.
2. M. FAHMY, M. J. PARK, M. TOMOZOWA and R. K. MACCRONE, *Phys. Chem. Glass* **13** (1973) 4.
3. *Idem, J. Amer. Ceram. Soc.* **276** (1971) 4.
4. M. FAHMY, PhD thesis, Michigan State University (1975).
5. L. D. BAGOMOLOVA, A. G. FEDEROV, V. A. JACHKIN and V. N. LAZUKIN, *J. Non-Cryst. Solids* **38/39** (1980) 159.
6. A. S. TENNY and J. WONG, *J. Chem. Phys.* **56** (1972) 5516.
7. K. J. MOE, *Phys. Chem. Glass* **6** (1965) 46.
8. P. E. JELLYMAN and J. P. PROCTER, *J. Soc. Glass Technol.* **175T** (1960).
9. A. SCOTT, B. L. ROBERT and K. D. DUDLEY, *J. Amer. Ceram. Soc.* **38** (1955) 10.
10. B. D. P. BUTTON, R. TANDON, C. KING, M. H. VELEZ, H. L. TULLER and D. R. UHLMANN, *J. Non-Cryst. Solids* **49** (1982).
11. B. C. NORMAN, H. D. LAWRENCE and E. W. STEPHEN, in "Introduction to Infrared and Raman Spectroscopy" (Academic Press, New York, 1964) p. 330.
12. M. IRION and M. COUZI, *J. Solid State Chem.* **31** (1980) 285.
13. M. TOMOZOWA, *Amer. Ceram. Soc. Special Pub.* **5** (1972) 41.
14. T. NISHIDA, T. SHIOTSUKI and Y. TAKASHIMA, *J. Non-Cryst. Solids* **43** (1981) 123.

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