AN INVESTIGATION OF THE EFFECT OF HEAT TREATMENT ON THE INCORPORATION OF IRON AS A NETWORK FORMER IN LITHIUM LEAD BORATE GLASSES

Dr. Jehad Mulhem*
Dr. Mohamed Muossa[+]
Dr. Ahmed Sanad[♣]

Abstract

Mossbauer spectroscopy was used to study the iron- containing borate glasses, polyalkaline borate glasses and also the effect of iron oxidation on the structure and electric properties lithium lead borate glasses. Investigation of the time effect of heat treatment on $25Li_2O$-$10PbO$-$65B_20_3$ based glass with addition of Fe_2O_3 up to 10mol%was performed. For 1mol% iron oxide up to 3mol% at different heat treatment (10, 20, 40, 70and 150 minutes) show quadruple doublet belongs to $Fe^{2+}$and Fe^{3+}as well as it become well resolved as the time of heat treatment increasing. In this case the iron enters the glass network as a modifier to form FeO_6 groups and Pb ions as a network former. At higher amount up to 10 mole % Mossbauer Spectra exhibit a superposition of quadruple doublet and sextet which referable to F_2O_3, and there are a transition from supper paramagnetic to ferromagnetic behavior. The iron ion exists in glass sample mainly in octahedral coordination rather than in tetrahedral coordination.

---

[*] **Professor At Department Of Physics, Faculty Of Science, Tishreen University ،Lattakia-Syria**

[+] **Associate Professor At Department Of Physics, Faculty Of Science, Tishreen University, Lattakia-Syria**

[♣] **Professor At Department Of Physics, Faculty Of Science, AL Azher University, Cairo-Egypt**

المعالجة الحرارية لاندماج الحديد كشبكة أساسية في زجاج بورات الرصاص والليثيوم

الدكتور جهاد ملحم*
الدكتور محمد موسى+
الدكتور أحمد سند♣

ملخص

استخدمت مطيافية مسباور لدراسة الحديد الموجود في الزجاج البوراتي، والزجاج البوراتي المتعدد الأساس، وأيضاً لدراسة تأثير أكسدة الحديد على التركيب والخواص الكهربائية لزجاجيات بورات الرصاص والليثيوم. تمت دراسة تأثير زمن المعالجة الحرارية على زجاج مكون من $25Li_2O-10PbO-65B_2O_3$ المضاف إليه تدريجياً أكسيد الحديد Fe_2O_3 حتى يصبح تركيزه 10 mol%. نتج عن المعالجات الحرارية عند إضافة (1-3 mol%) من أكسيد الحديد خلال الأزمنة (150− 70− 40− 20− 10) دقيقة، ظهور زوج رباعي أقطاب كهربائي يعود إلى كل من Fe^{+2}، Fe^{+3}، وأصبح ذلك أكثر وضوحاً عند زيادة زمن المعالجة الحرارية. في هذه الحالة، يدخل الحديد إلى الشبكة البلورية كمعدّل لتشكيل مجموعات Fe_2O_6 وأيونات الرصاص كشبكة أساسية. عند إضافة كمية أكبر من أكسيد الحديد بتركيز 10mol%، فإن طيف مسباور يظهر تطابقاً لزوج رباعي وسداسي أقطاب كهربائي يعزى ذلك لوجود Fe_2O_3، كما يحدث انتقال من حالة الحديد عالي المغنطة إلى حالة الحديد عادي المغنطة. تم التأكد من أن أيون الحديد يتواجد في عينة الزجاج بشكل رئيسي في التنسيق ثماني الوجوه أكثر منه في التنسيق رباعي الوجوه.

---

[*] أستاذ في قسم الفيزياء من كلية العلوم بجامعة تشرين، اللاذقية–سورية

[+] أستاذ مساعد في قسم الفيزياء من كلية العلوم بجامعة تشرين، اللاذقية–سورية

[♣] أستاذ في قسم الفيزياء من كلية العلوم بجامعة الأزهر، القاهرة–مصر

1. Introduction

Iron-containing borate glasses have been the object of quite high number of Mossbauer studies [1-31]. For most elementary glasses in the B_2O_3-Fe_2O_3 system with Fe_2O_3 concentration ranging from 0.0028 to 0.05 mass fractions, the result was obtained that Mossbauer spectrum of ^{57}Fe shows a superposition of quadrupole doublet, and a magnetic sextet [21]. Of greatest interest studies of the glass in the R_2O-B_2O_3-Fe_2O_3 system (where R_2O=Li_2O, Na_2O, K_2O). Raman et al. (5, 9, 11, 16, and 18) have made a Mossbauer study of R_2O-B_2O_3-Fe_2O_3 glasses aimed to detecting unbounded oxygen. For $xR_2O.(94-x)$ B_2O_3-$6Fe_2O_3$ (where x is mole %) glasses the Mossbauer spectra taken at room temperature showed quadrupole doublets whose isomer shift gradually decrease with increasing concentration of the alkali metal over the range 0-20 mole% R_2O. This decrease becomes rather drastic at 22 mole%. It was concluded that iron as Fe^{3+} is incorporated into the glass structure network, and with varying x the polyhedron of oxygen atoms surrounding the Fe^{3+} ion changes from octahedral to tetrahedral. This structural change is due to non-bridging oxygen in alkali concentration ranges beyond 20 mole%.

Polyalkaline borate glasses are the object of Mossbauer investigations reported in [4, 13]. It is shown that in wLi_2O. (0.35-w) PbO $0.1Fe_2O_{3w}$. $0.55B_2O_3$ (where w is the mass fraction ranging from 0 to 0.12) glasses iron stabilizes as Fe^{2+} and Fe^{3+}, the contribution of Fe^{2+} decreasing with the growth of w and becoming zero at w = 0.117 [13].Several methods [32] were studied the effect of iron oxide addition on the structure and magnetic and electric properties of lithium lead borate glasses. Those methods such as IR transmission spectra, optical absorption techniques, electrical conductivity, magnetic susceptibility measurements and differential thermal analysis (DTA) have been used to obtain information about whether the iron ions occupy the Fe_2O_3 to the glass samples. The authors [32] found from those measurements that the addition of up to 3mole% iron oxide to the samples introduced as modifiers at the expense of Pb ions. The iron enters the glass structure as network former with a FeO4 structure. Moreover, they suggest that for high amount of iron oxide, the iron ions exist in an octahedral coordination rather than in tetrahedral coordination.

The effect of adding Fe_2O_3 to Li_2O-B_2O-PbO glass system on the crystallization kinetic parameters has been studied [33]. They found that at low Fe_2O_3 up to 3 mol% the iron ions presence in an octahedral coordination enter as a network modifier which is high agent for crystallization and causing a decrease in the activation energy. For a higher amount, the iron ions tend to form a tetrahedral coordination and to increase the activation energy.

Also they observed that the heat treatment caused an increase in non- bridging oxygens.

2. Experimental

A series of glasses was prepared by adding 1, 2, 3, 5 and 10 mole% Fe_2O_3 to $25Li_2O$-$10PbO$-$65B_2O_3$ mole% based glass. The glasses were melted at 1423±20Kfor one hour, and then quenched in air at room temperature between two copper plates. All glass samples were heat treated for 10, 20, 40, 70 and 150 minutes at $T=T_p=843K$ (Tp is the peak temperature as determined from DTA measurements for a heating rate of 30 C^o/min. The heat treated samples were crushed to powder form. The Mossbauer measurements were performed by constant acceleration method at room temperature, with a source of cobalt-

57 (100 mCi) diffused into an Rh matrix. The velocity of the spectrometer was calibrated using an iron metal absorber which was also used as a reference for the isomer shift value.

3. Results and discussion

Investigation of the time effect of heat treatment on $25Li_2O$-$10PbO$-$65B_2O_3$ mole% based glass with addition of Fe_2O_3 up to 10 mole% was performed.

Fig.1 shows the Mossbauer spectra for the glass samples of 1 mole% iron oxide at different times of heat treatment (10, 20, 40, 70 and 150 minutes), starting by the glass sample. All spectra show quadrupole doublets belonging to Fe^{2+} and Fe^{3+} as well as it becomes well resolved as the time of heat treatment increases. On the other hand, the isomer shifts for Fe^{3+} increase gradually with increasing the heat treatment time up to 70 min. After that it decrease again, this indicates that Fe3+ incorporated into the glass structure network. Moreover, this drastic decrease occurred in the isomer shift is believed to be induced by a change in the Coordination State of Fe^{3+} ions owing to the presence of non-bridging oxygen.

Fig.2 and Fig.3 show the Mossbauer spectra for the glass samples but with addition of 2 and 3 mole % iron oxide, respectively. All the spectra exhibit the same behavior as in Fig.1. The only difference is the intensity which has a minimum relative fraction of Fe^{3+} at 3 mole% Fe_2O_3 for all times of heat treatment and this going with the conductivity result [32] which has a minimum at 3 mole% iron oxide.

The interesting feature is observed when going further than 3 mole% up to 10 mole% Fe_2O_3. Indeed, the Mossbauer spectra exhibited a superposition of a quadrupole doublet and a sextet which is referable to the phase Fe_2O_3. This feature is more clearly visible at 10 mole% iron oxide (Fig.5) which shows the transition from superparamagnetic to ferrimagnetic behaviour.

The spectra consists of a magnetically split sextet component and a central doublet. This sextet has a magnetic hyperfine field splitting and isomer shift belonging to the phase Fe_2O_3 (hematite) for Fe^{3+} cation in octahedral site. As the time of heat treatment increases the intensity of the magnetic component increases and simultaneously the doublet component, which appears in the center of the spectrum, decreases in intensity. This behaviour indicates clearly that the magnetic sextet and the doublet components both arise from the same species, which exhibit superparamagnetism. It can be concluded that at lower amount of iron oxide up to 3 mole%, the iron ions enter the glass network as a modifier to form FeO_6 groups and Pb ions as a network former. At higher amount of iron oxide, more than 3 mole% up to 10 mole%, the iron ions enter the glass structure as a network former and modifier. Moreover, at that high rate of iron content, the iron ions exist in the glass samples, mainly in octahedral coordination rather than in tetrahedral coordination. Also, as shown from Mossbauer spectra at 10 mole%, the increasing in non-bridging oxygen which is responsible for the separation of the hematite phase and existence of Fe^{3+} as a network former in the glass samples, not only concentration of iron oxide dependence, but also time of heat treatment dependent.

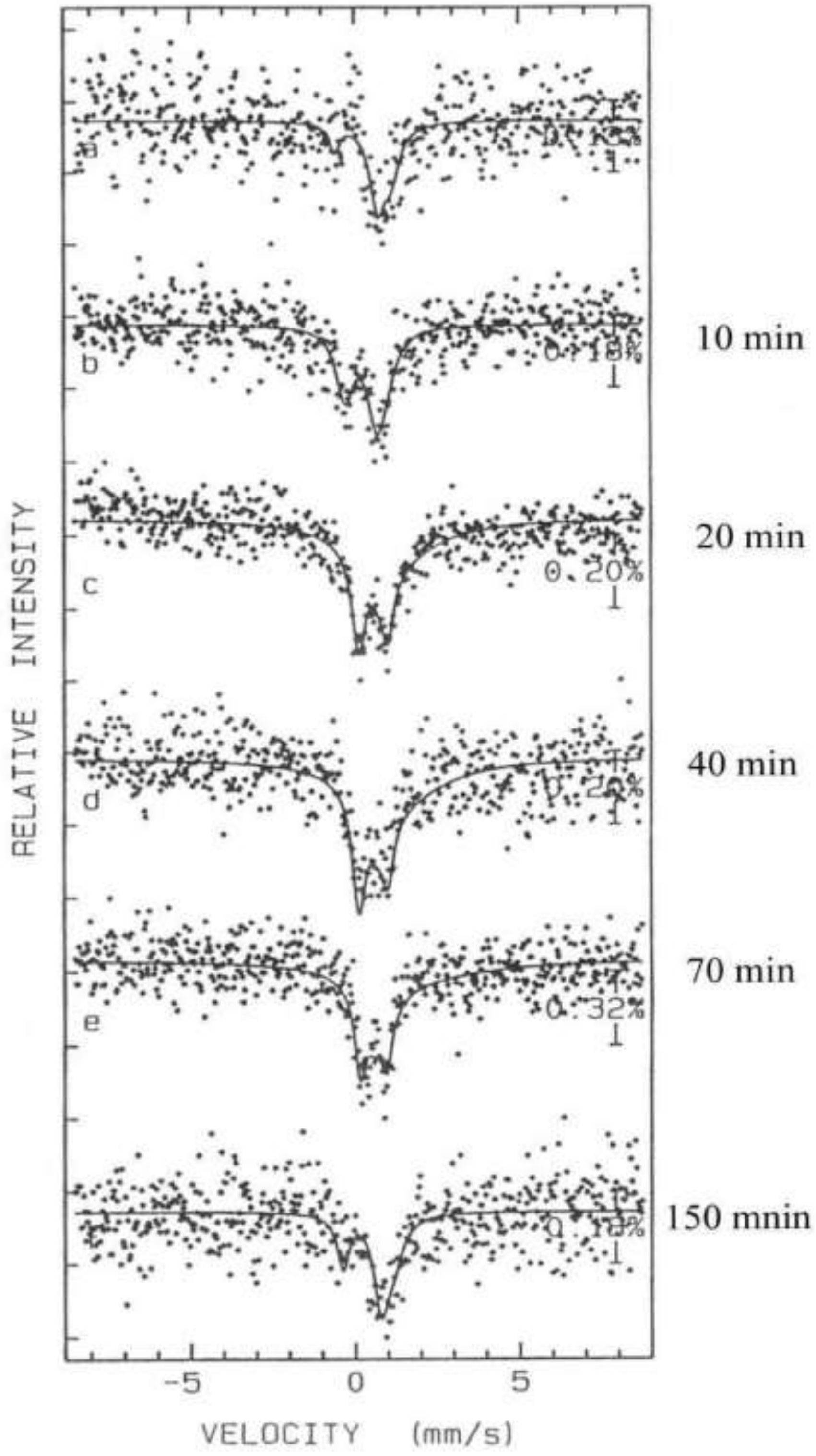

Fig.1. The Mossbauer spectra at room temperature of the glass samples heat treated at 843 k Containing 1mol% iron oxide, (a) glass sample, b) 10 min., c) 20 min., d) 40 min., e) 70 min. and f) 150 min.

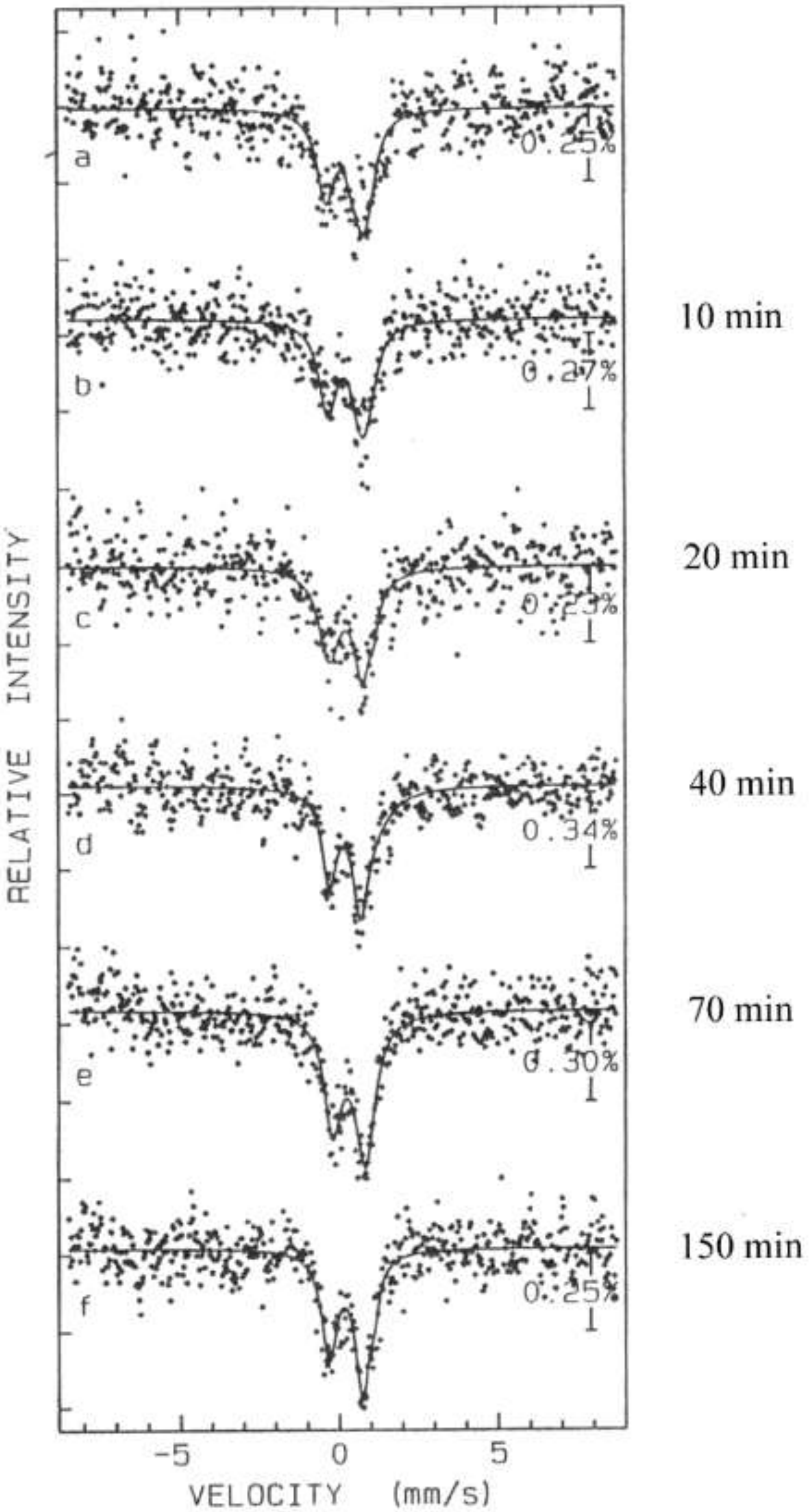

Fig.2. The Mossbauer spectra at room temperature of the glass samples heat treated at 843 k Containing 2mol% iron oxide, (a) glass sample, b) 10 min., c) 20 min., d) 40 min., e) 70 min. and f) 150 min.

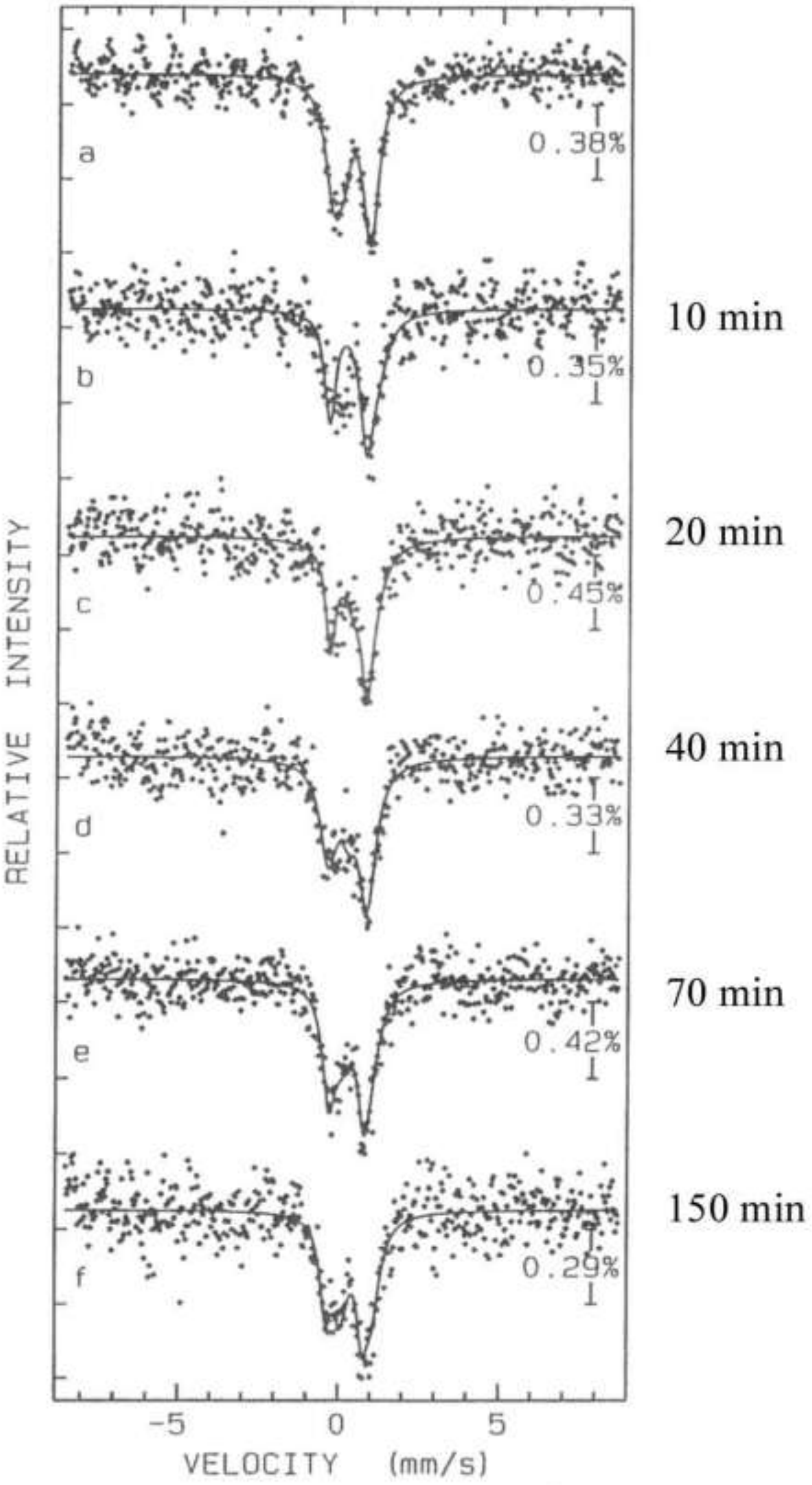

Fig.3. The Mossbauer spectra at room temperature of the glass samples heat treated at 843 k Containing 3mol% iron oxide, (a) glass sample, b) 10 min., c) 20 min., d) 40 min., e) 70 min. and f) 150 min.

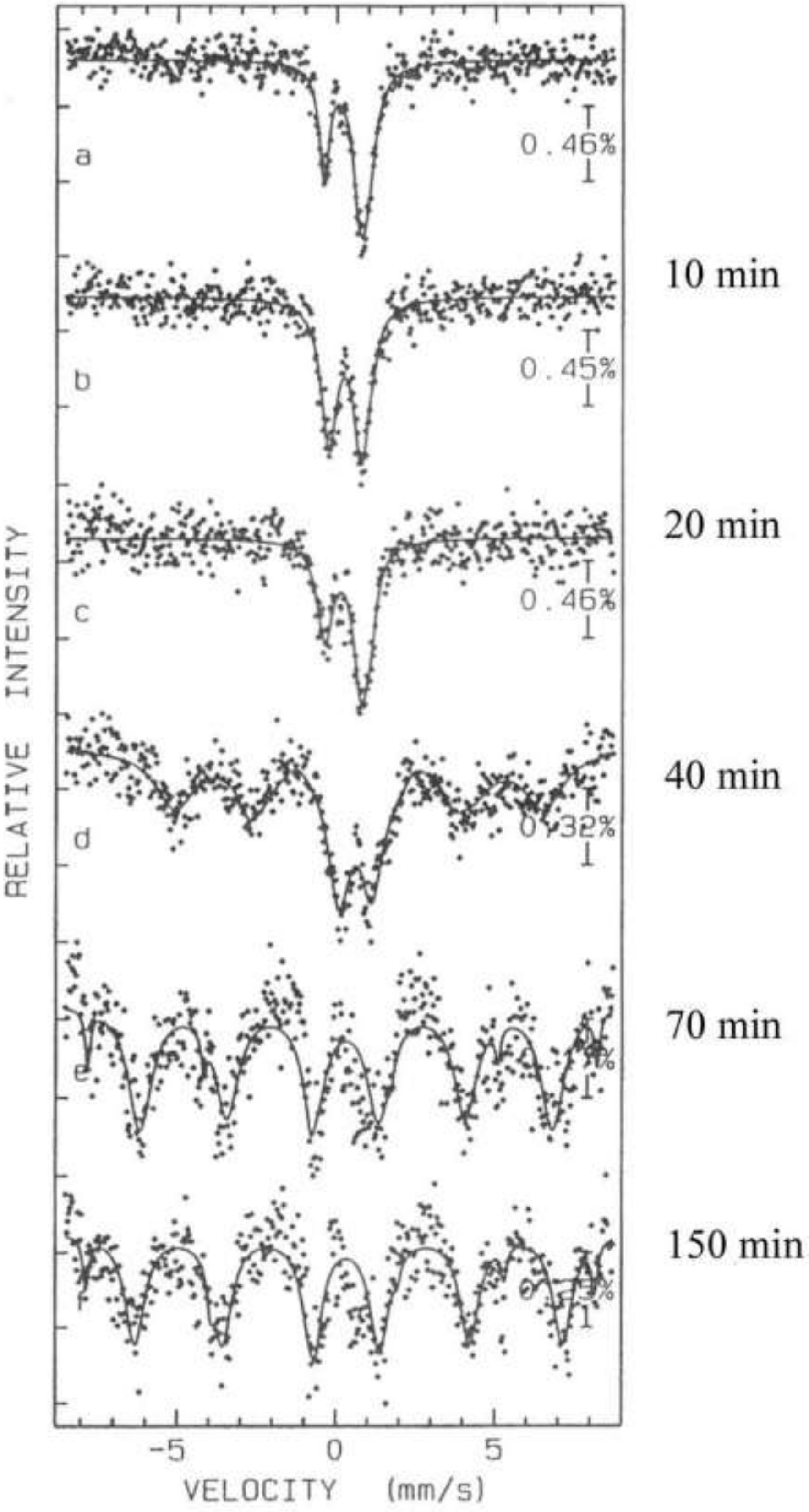

Fig.4. The Mossbauer spectra at room temperature of the glass samples heat treated at 843 k Containing 5mol% iron oxide, (a) glass sample, b) 10 min., c) 20 min., d) 40 min., e) 70 min. and f) 150 min.

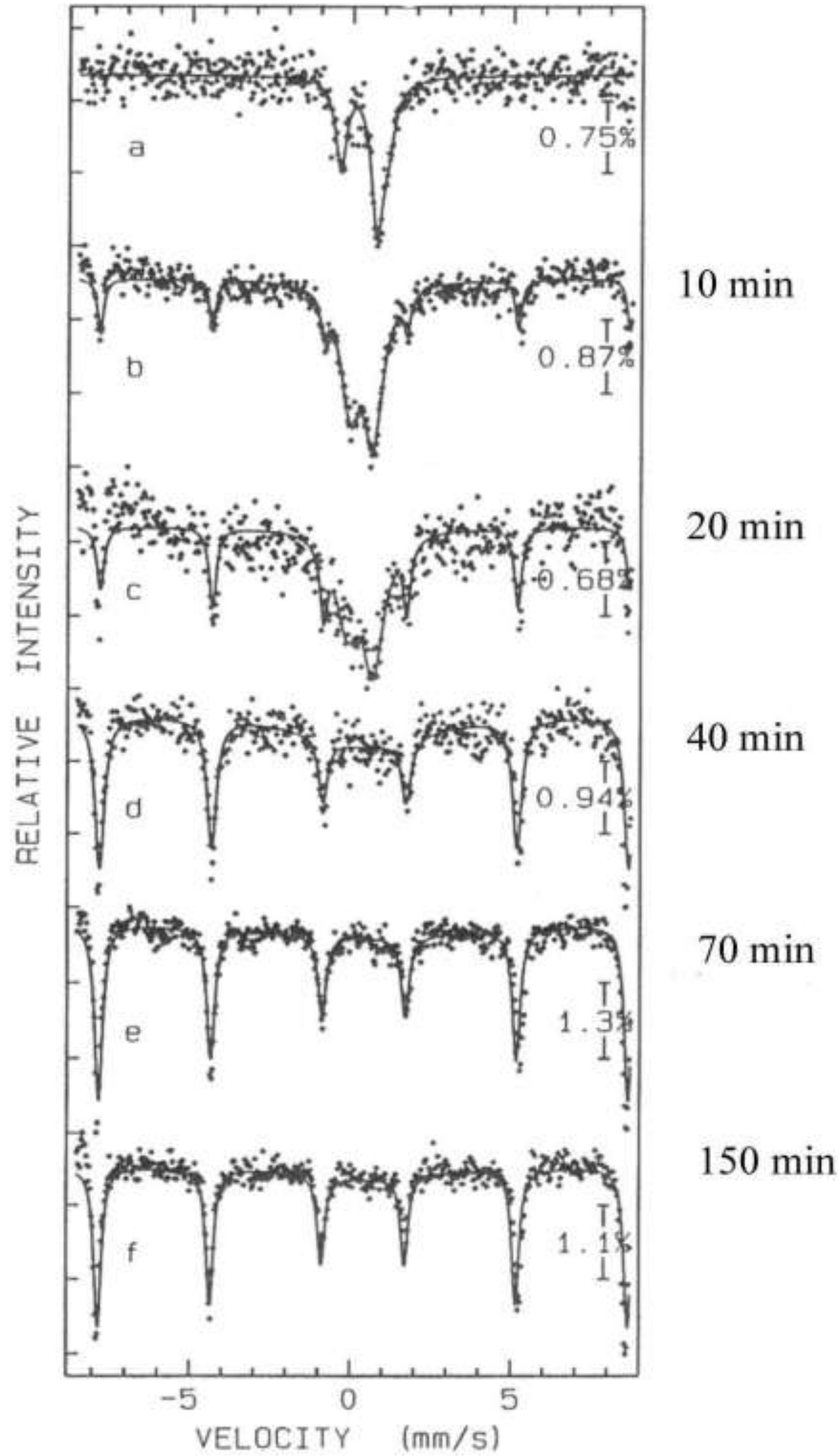

Fig.5 The Mossbauer spectra at room temperature of the glass samples heat treated at 843 k Containing 10mol% iron oxide, (a) glass sample, b) 10 min., c) 20 min., d) 40 min., e) 70 min. and f) 150 min.

4. Conclusion

- MÖssbauer spectroscopy was used to study the iron- containing borate glasses, polyalkaline borate glasses and also the effect of iron oxidation on the structure and electric properties lithium lead borate glasses.
- Investigation of the time effect of heat treatment on $25Li_2O$-10Pb0-$65B_20_3$ based glass with addition of Fe_2O_3 up to 10mol%was performed.
- For 1mol% iron oxide up to 3mol% at different heat treatment (10, 20, 40, 70and 150 minutes) show quadruple doublet that belongs to$Fe^{2+}$and Fe^{3+} as well as it becomes well resolved as the time of head treatment increases. In this case the iron enters the glass network as a modifier to form FeO_6 groups and Pb ions as a network former.
- At higher amount up to 10 mole % Mossbauer Spectra exhibit a superposition of quadruple doublet and sextet which is referable to Fe_2O_3, and are characteristic of a transition from supper paramagnetic to ferrimagnetic behavior. Here iron ion exists in glass sample mainly in octahedral coordination rather than in tetrahedral coordination.
- Increasing in non-bridging oxygen which is responsible for the existence of Fe^{3+} as a net work former in the glass sample, depends on the concentration of iron oxide and time of heat treatment.

REFERENCES

1. Bukrey, R., Kenealy, f., Beard, g. and Hooper, H., J. Appl. Phys., 40, 4289 (1969).
2. Bukrey, R., Bull. Amer. Ceram. Soc., 51, 371 (1972).
3. Jach, J., J. Nonmetals, 1, 1559 (1973).
4. Jach, J., J. Nonmetals, 2, 89 (1974).
5. Raman, T., Nagesh, V. K., Chakravorty, D. and rao, G. N., Internat. Conf Hyperfine Interact. Stud. Nucl. React. And Decay, Uppsala, P. 280 (1974).
6. Saini, M. S. and Kamal, R., J. Non-cryst. Sol., 87, 103 (1986).
7. Trieher,M. J., Thomos, J., Omer, M. H., Osman, A. and Bishay, A., J. Mater. Sci., 9, 1115 (1974).
8. Yuanfa, H. and Rongchuan, L., Hyperfine Interactions, 27, 285 (1985).
9. Raman, T., Nagesh, V. K., Chakravorty, D. and rao, G. N., J. Appl. Phys., 46, 972(1975).
10. Maccronel, R. K., Williams, J., Kim, K. and Maley, M. P., The Structure of Non-crystalline materials, London, 1977, P. 121.
11. Barb, D., Nicula, A., Tarima, D. and Baican, K., Proc. Intern. Conf. Mossbauer Spectroscopy, Bucharest-Romania, 1977, Vol. 1., p.425.
12. Burze, E. and Ardelean, I., Proc.Intern. Conf. Mossbauer Spectros- copy, Bucharest-Romania, 1977, Vol. 1., p. 245.
13. Ardelean, I., Burzo, E. and Pop, I., Sol. State Commun., 23, 211 (1977).

14. Raman, T., Rao, G. and Chakravorty, D., Hyperfine Interact., 4, 873 (1978).

15. Sekhon, S. S. and Kamal, R., J. Non-cryst. Sol., 28, 189 (1978).
16. Raman, T., Rao, G. and Chakravorty, D., J. Non-cryst. Sol., 29, 85 (1978).
17. Horie, O., Syono, Y., Nakagama, Y., Ito, A., Okamura, K. and Yakajima, S., Sol. State Commun., 25, 423 (1978).
18. Danheim, H. and Frey, T., Borate glasses: structure, properties, application, eds Pye, L. D., Frechette, V. D., Kreidl, N. J., Plenum-press, N-Y, p.227, (1978).
19. Sekhon, S. S. and Kamal, R., J. Appl. Phys., 49, 3444 (1978).
20. Syono, Y., Ite, A. and Horie, O., J.Phys. Soc. Jap., 46, 793 (1979).
21. Syono, Y., Ite, A. J. Physique Colloque, 40, C2-115 (1979).
22. Sekhon, S. S. and Kamal, R., J. Non-cryst. Sol., 33, 169 91979).
23. Burze, E. and Ardelean, I., Phys. Chem. Glasses, 20, 15(1979).
24. Friedt, J. M., J. Physique, 41, 273 (1980).
25. Nishida, T. and Takashima, Y., J. Non-cryst.Sol., 37, 37 (1980).
26. Nishida, T., Shiotsuki, T. and Takashima, Y., J. Non-cryst. Sol., 41, 161 (1980).
27. Nishida, T., Hirai, T. and Nakayama, N., Radiochem. Radioanal. Lett., 42, 189 (1980).
28. Chaumont, C., Derory, A. and Bernier, J. C., Mater. Res. Bull., 15, 771 (1980).
29. Nishida, T., Hirai, T. and Takashima, Y., J. Non-cryst. Sol., 43, 221 (1981).
30. Kishore, N., Bansal, T. K. and Kamal, R., J. Non-cryst. Sol., 69, 213 (1985).
31. Kashif, I., Farouk, H., Soliman, A., Aly, S. A., Zahr El-Deen, H. and Sanad, A. M., Material Science and Engineering B38, p.217 (1996).
32. Kashif, I., Zahr El-Deen, H., Farouk, H., Soliman, A. A., Aly, S. A. and Sanad, A. M., Egypt. J. Sol., Vol. 19, No. 2, (1996).
33. Kashif, I., Aly, S. A., Soliman, A. A. and Sanad, A. M., Al Azhar Bull. Sci. Vol. 8, No. 2, p. 493 (1997).
34. Kashif, I., Abo El- Azem, A. M., Gomaa, S. Sh. And Sanad, A. M., Phys. Chem. Glasses, 30 (5) 167 (1989).